

### HAZARDOUS CONTAMINANTS PROGRAMME

ENVIRONMENTAL ASPECTS OF SELECTED

CHLORINATED HYDROCARBONS IN ONTARIO

# A COMPREHENSIVE BACKGROUND REPORT HCP-2-78

ARB-TDA-33-80

November 1978



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HCP-2-78

Prepared For

Air Resources Branch
Ontario Ministry of the Environment

by

United Technology and Science Inc.

November, 1978

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4 SUMMARY

#### 4 SUMMARY

The chlorinated hydrocarbons considered in this report are:

- methyl chloride
- methylene chloride
- chloroform
- carbon tetrachloride
- dichloroethane
- trichloroethane
- tetrachloroethane
- dichloroethylene
- trichloroethylene
- perchloroethylene
- chloroprene
- chlorobenzene
- dichlorobenzene

#### Chemical and Physical Properties

Introduction of varying amounts of chlorine into a hydrocarbon, such as methane, ethane, ethylene, or benzene, yields a wide variety of liquids and gases whose properties can be generally graded according to their degree of chlorination. In general, the physical properties of the chlorinated hydrocarbons change progressively with increase in the number of chlorine atoms substituted into the methane, ethane, and ethylene molecule. Thus, the chlorinated derivatives of these simple aliphatic hydrocarbons show a progressive increase in density and

viscosity with increasing chlorine content, while the properties of specific heat, dielectric constant and solubility in water show a corresponding progressive decrease. Several exceptions to these general trends exist. For example, chloroform is more water-soluble than either methyl chloride or methylene chloride. Chlorinated benzenes show more complex relationships between chlorine content and properties.

The major properties of technological interest introduced to hydrocarbons by chlorination are solvation power, viscosity, reduced flammability and chemical reactivity.

Chlorinated aliphatic hydrocarbons normally undergo nucleophilic substitution reactions, elimination reactions, exchange reactions, and addition reactions across double bonds.

Chlorinated benzenes generally undergo the same types of reactions as nonchlorinated aromatic hydrocarbons, but require more vigorous conditions because of the deactivating effect towards further substitution of the chlorine substituents on the aromatic nucleus.

#### Major Producers, Uses, and Market Forecasts

Publicly available information on production and markets specific to Ontario for the compounds of interest here is very limited since, for most of the compounds, there are only one or two manufacturers of these compounds and therefore figures are not released for reasons of confidentiality.

Methyl chloride is not currently manufactured in Ontario but it is imported and marketed by Dow Chemical Co. Ltd. in Sarnia. Annual usage

in Canada for 1975 is estimated to be about 10 Gg. Its main use is as a blowing agent in the production of foamed plastics, in the manufacture of methyl- and carboxy-methyl-cellulose, as a catalyst solvent in butyl rubber manufacture, and in the manufacture of tetramethyllead. Its use as a refrigerant and grain fumigant are of minor importance.

Methylene chloride is not manufactured in Canada but Dow Chemical Co. Ltd. in Sarnia imports the crude product for purification and marketing. The estimated usage for 1976 in Canada is about 10 Gg. Methylene chloride is used extensively in paint stripping and cold degreasing formulations. It is also used as a vapor degreaser. Other uses of methylene chloride are in aerosol formulations; in the extraction of heat-sensitive substances in food processing such as edible fats, cocoa butter, and the beer flavoring in hops; in the manufacture of photographic film where it is used as a polymer solvent; as a solvent for cellulose triacetate in rayon yarn manufacture; in the production of PVC fiber; and as a low temperature heat transfer medium. Methylene chloride is also used to clean reactors producing polyurethane.

Chloroform is not manufactured in Ontario but it is imported for use and marketing by Dow Chemical Co. Ltd. in Sarnia. Reported imports for 1976 are 2.8 Gg. The major use is for the production of chlorodifluoromethane. It is also used as a solvent in specialty formulations (eg fumigants, insecticides, and fungicides).

<u>Carbon tetrachloride</u> is manufactured in Ontario by Dow Chemical Ltd. in Sarnia and Canadian Industries Ltd. in their subsidiary plant in

Cornwall. Production for 1974 is estimated to be 30 Gg. The major use is for the manufacture of chlorofluoromethanes by Allied Chemical, Amherstburg, and DuPont of Canada Ltd., Cornwall. It is also used in specialty formulations such as grain fumigants and solvent applications. Due to the reduced use of chlorofluorocarbons as an aerosol propellant, the production of carbon tetrachloride is expected to drop to about 20-25 Gg/annum by 1980.

Ethylene dichloride is produced in Ontario by Dow Chemical of Canada Ltd. in Sarnia and Ethyl Corp. Ltd. in Corunna. Dow has an estimated production capacity of 135-180 Gg/annum and Ethyl Corp. of about 5 Gg/annum. Ethyl Corp. uses ethylene dichloride as a gasoline additive. Dow uses most of its ethylene dichloride production for the manufacture of vinyl chloride. Other uses by Dow include production of methyl chloroform and in grain fumigant formulations.

Methyl chloroform is produced in Ontario by Dow Chemical of Canada Ltd. in Sarnia. The estimated production capacity is 15-20 Gg/annum. The major use of methyl chloroform is as a vapor degreaser and as a cold cleaning solvent. Other uses include as a solvent in contact and rubber cements and in some paints. Usage as a vapor degreaser is expected to grow at about 10 %/annum.

Tetrachloroethane is not manufactured or used in Ontario.

Vinylidene chloride is not manufactured or used in Canada.

<u>Trichloroethylene</u> is not manufactured in Ontario but it finds a major use as a vapor and cold degreasing solvent and dry-cleaning solvent.

Minor applications are as an extractant for naturally occurring substances, such as waxes and greases from cotton and wool, and caffeine from coffee beans. It has also been used as a low temperature heat-transfer medium and as a component of rust prevention formulations.

Canadian usage for 1975 is estimated to be about 18 Gg/annum. Due to suspected adverse health effects and photochemical reactivity the usage of trichloroethylene is expected to decline.

Perchloroethylene is produced in Ontario by Dow Chemical of Canada Ltd. at Sarnia. The 1974 Dow production is estimated to be about 17 Gg. The major use of perchloroethylene is as a dry-cleaning solvent. It is also used as a metal degreasing solvent, in the extraction of fats, and other specialty solvent purposes. One special-purpose application is in the electro-winning plant of Inco Ltd. where hot perchloroethylene is circulated to remove sulfur. The demand for perchloroethylene is expected to rise slowly over the next few years.

Chloroprene is not manufactured or used in Canada.

<u>Chlorobenzene and dichlorobenzene</u> are not produced or used in Ontario.

#### Process Descriptions

In Ontario, carbon tetrachloride is manufactured by the chlorination of propane. Tetrachloroethylene is produced as a co-product. Chlorine, propane and recycle organic chlorides are fed as vapors to the reactor at a temperature of 550 °C to 700 °C. The reactor effluent, which consists mainly of carbon tetrachloride, tetrachloroethylene, excess chlorine and HCl, is quenched with tetrachloroethylene. The rapid quench preserves the equilibrium ratio obtained in the reactor and

prevents the formation of undersirable by-products. Products are recovered by distillation and a water scrub to remove HCl. The major potential source of emissions is from the purge on the dry chlorine recycle.

The compounds ethylene dichloride and vinyl chloride are manufactured in Ontario by an integrated process. Ethylene dichloride is produced using direct chlorination of ethylene by chlorine, with a catalyst, in the vapor phase by the use of a refluxing reactor at 90 °C and about 50 kPa. The ethylene dichloride is purified by fractional distillation and fed to a pyrolysis furnace where it reacts to form vinyl chloride and HCl. The products are separated and the HCl is sent to an oxyhydrochlorination process to produce ethylene dichloride. In this process, HCl, ethylene and air are fed to a reactor using either a fixed or fluid catalytic bed. The products (water and ethylene dichloride) are recovered by condensation and separated by either solvent adsorption or refrigerated condensation. The crude ethylene dichloride is purified by distillation and fed to the vinyl chloride production stream. main emission source is from the oxyhydrochlorination process through the vent on the ethylene dichloride secondary separator. Emissions also occur in the direct chlorination process from the vent on the reflux condensor. Effluent discharges occur from the gas scrubbers in the purification system. Solid wastes are generated from the filter of the purification system and from bottoms of distillation columns.

l,l,l-trichloroethane is produced in two steps from vinyl chloride.

Vinyl chloride is mixed at 40 °C with recycled l,l,l-trichloroethane

and HCl in a hydrochlorinator tower with a catalyst. The vinyl chloride reacts with HCl to form 1,1-dichloroethane. The effluent from the hydrochlorinator is decanted from the catalyst then the chlorine content of the products is adjusted by a photochemical chlorinator followed by separation by steam distillation, condensation and distillation. Product 1,1-dichloroethane vapor and chlorine are fed to a tower reactor at 400 °C and atmospheric pressure in which 1,1,1-trichloroethane and HCl are formed. These are then cooled and fed to the hydrochlorinator. The main source of emissions from this process is through the vent on the hydrochlorinator and the purge on the 1,1-dichloroethane line.

Tetramethyl lead is manufactured in Ontario using the batch alloy process. Methyl chloride is added to an autoclave containing a lead-sodium alloy. Vapors are vented from the autoclave and into a reflux condensor then returned to the autoclave. After 30 to 60 minutes the autoclave is vented and the products discharged into a steam still. The tetramethyl lead is separated by direct steam stripping, condensed and decanted. The major sources of potential emissions are from the vent on the autoclave and from the venting of blanket gases used during transfer operations from the autoclave to the still. The major source of effluent discharge is from the decanter.

A large portion of the chloroform and carbon tetrachloride in Ontario is used to manufacture chlorofluorocarbons. This is carried out by mixing the chlorinated hydrocarbon with hydrofluoric acid and a catalyst by either a batch or continuous operation. The degree of fluorination is controlled by temperature and pressure. The products are purified by distillation, scrubbed, and dried. The main source of emissions is from the vent on the distillation column.

#### Emission and Discharge Control Technology

Air emission control systems are usually an integral part of manufacturing technology. As a consequence, process data are considered proprietary, and are not usually available to the public. Condensation, absorption, adsorption and incineration are the most frequently used control systems. A multistage condensation system with refrigeration in the final stage can achieve a 99+ % removal efficiency for the compounds of interest here. Water, mineral oils, non-volatile hydrocarbon oils and various aqueous solutions are used for the absorption of hydrocarbons. Absorption systems can be designed to achieve up to 95 % removal efficiency. Adsorption on the surface of specially prepared granular solids, and adsorbents, is a very efficient method for selective removal of hydrocarbons from gaseous streams. Activated charcoal is the most widely used adsorbent. Incineration is frequently used in the petrochemical industry. A retention time of 2 seconds at 1000 °C is considered satisfactory for the destruction of most organics. Flares are not considered as environmentally satisfactory for the disposal of hazardous gases because of incomplete combustion and noise pollution problems.

A major source of hydrocarbon losses is during storage and transfer operations. The use of floating roofs, vapor recovery units and reduction of fugitive emissions (pump seals, relief valves, etc.) could considerably reduce these losses.

Removal of hydrocarbons from <u>water</u> discharges requires several steps and includes primary nonsolubilized hydrocarbon removal followed by solubilized hydrocarbon removal. Biological oxidation is used, although

for the compounds of interest it is a slow process. A complete removal of hydrocarbons from waste water effluents can be achieved by:

- primary treatment such as gravity oil-water separation and, induced air flotation (IAF), dissolved air flotation (DAF) or filtration followed by
- the series: biological oxidation carbon adsorption treatment or
- the series: carbon adsorption biological oxidation treatment or
- carbon adsorption as the only treatment

Other available technologies are steam stripping, solvent extraction, membrane processes and wet air oxidation.

Waste disposal by incineration is an ultimate disposal method if properly designed and operated. A residence time of 2 seconds at 1000 °C is considered adequate for most organic compounds. Incomplete combustion of chlorinated compounds may result in emissions of phosgene and hydrogen chloride Excess hydrogen is required to form HCl which can be recovered. Deep wells and land fill sites have often been used in the past but sites are becoming more and more difficult to find where there is no risk of ground water contamination.

#### Sampling and Analysis

Occupational atmospheres have been sampled for these compounds using various methods such as grab samples in plastic bags or other containers, absorption in impingers, and adsorption on such sorbants as silica gel or activated charcoal, etc. Analytical methods include such techniques as colorimetry, infrared and ultraviolet spectroscopy and gas chromatography. The most widely accepted method in North America (recommended by NIOSH and



OSHA) is sampling by adsorption on activated charcoal, followed by desorption with carbon disulfide and analysis by gas chromatography (GC).

Ambient atmospheres are more difficult to sample and analyse due to the low concentrations of the compounds of interest and because of the large number of other compounds frequently present in admixture.

Many sampling methods have been used such as grab sampling in plastic, glass, or stainless steel containers. Enrichment methods such as condensation, absorption and adsorption have been used. The best technique, at the present time, appears to be adsorption on Tenax GC followed by thermal desorption into a GC equipped with a mass spectrometer for compound identification. Care must be taken not to exceed the breakthrough volume of the Tenax adsorbent during sampling. The best choice of columns appears to be glass support-coated capillary columns.

Methods of sampling water for chlorinated hydrocarbons have included solvent extraction, activated carbon adsorption followed by solvent extraction, head space analysis and inert gas stripping. The most widely accepted method of analysis is gas chromatography.

#### Environmental Persistence and Fate

The major degradation pathway for the compounds of interest here is probably atmospheric photooxidation - regardless of the media in which the primary emissions occur. Studies have shown that evaporative half lives of these compounds from aqueous discharges is relatively short (less than about seven hours for the longest case). There does not appear to be any significant accumulation of these compounds in sediments.

Although biological degradation of these compounds can take place, it is

a slow process and does not compete with evaporation. Also, with the possible exception of chloroprene, hydrolysis and aqueous oxidation do not take place at a significant rate.

The chlorinated olefins of interest here are sufficiently reactive in the atmosphere that they can take part in photochemical reactions on a local scale. The other compounds, however, are much less reactive and are not expected to take part in photochemical smog formation on a local scale. Degradation of these less reactive chlorinated hydrocarbons takes place on a regional or global scale. The relative reactivities of various chlorinated hydrocarbons in the atmosphere have been studied by a number of workers. The compounds of interest here are listed below in order of decreasing reactivity. This ordering may vary somewhat from study to study depending on conditions used, etc. However, the general trends are as listed.

$$\begin{array}{l} {\rm CH_2 = CC1 - CH = CH_2} \ > \ {\rm CHC1 = CC1_2} \ > \ {\rm CHC1 = CHC1} \\ > \ {\rm CH_2 = CC1_2} \ > \ {\rm Ø - C1} \ > \ {\rm Ø - C1_2} \ > \ {\rm CC1_2 = CC1_2} \\ > \ {\rm CHC1_2 - CHC1_2} \ > \ {\rm CH_2 C1 - CC1_3} \\ > \ {\rm CHC1_2 - CH_2 C1} \ > \ {\rm CHC1_3} \ > \ {\rm CH_2 C1_2} \ > \ {\rm CH_2 C1 - CH_2 C1} \\ > \ {\rm CH_3 C1} \ > \ {\rm CH_3 - CC1_3} \ > \ {\rm CC1_4} \\ \end{array}$$

In addition to industrial sources of chlorinated hydrocarbons through discharges, it has been demonstrated that organohalides can be formed during water treatment by chlorination. It appears that fulvic and humic acids may act as precursors. In Ontario, studies have shown that, in potable water, chloroform is the predominant organohalide and concentrations range from 1 ppb or less up to 159 ppb. Reported

concentrations of organohalides in water courses are highly variable, however, elevated levels are usually associated with local industrial activity.

Numerous studies of ambient air concentrations of chlorinated hydrocarbons have been reported over the last few years. Much of this work has focused on the effect of chlorinated compounds on stratospheric chemistry. Global background concentrations as well as urban concentrations in heavily industrialized areas have been studied.

In the U.S., studies in a number of areas of high concentration of chemical and industrial activity report ambient concentrations of almost all of the compounds of interest here at levels ranging from ppt to ppb. Most compounds could be identified with a particular industrial activity near the sampling site. Similar results have been reported from studies in other countries.

Hemispheric background concentrations have been estimated for a number of chlorinated hydrocarbons. Significant concentrations for methyl chloride, methylene chloride, chloroform, carbon tetrachloride, methyl chloroform, trichloroethylene, and perchloroethylene are reported.

Concentrations (in the northern hemisphere) range from 15 ppt for trichloroethylene to about 700 ppt for methyl chloride. It is of interest to note that methyl chloride is the largest carrier of chlorine in the atmosphere followed by carbon tetrachloride. Also, despite the relatively high atmospheric reactivity of tri- and perchloroethylene, they are still present in background air at concentrations of around 15-20 ppt due to their high volume usage.

With the exception of carbon tetrachloride, the other chlorinated hydrocarbons present in background air show strong inter-hemispheric gradients indicating significant anthropogenic sources. A large natural marine source of methyl chloride has been suggested. It is not clear whether or not carbon tetrachloride has a significant natural source. It has been speculated that chloroform, carbon tetrachloride and perhaps other chlorinated hydrocarbons may be formed through atmospheric reactions There is no direct evidence to indicate that this does occur in the atmosphere.

#### Health Effects

The following is a brief summary of biological information for each compound of interest. Included is a three category toxicity rating (A, B and C) for each compound. The selection of such a cryptic rating system contains a considerable degree of subjective judgement. It is important to keep in mind that the data upon which the categories are based are very seldom complete and/or are often not of a uniformly high quality. Due to this, and a number of other qualifying factors (described in detail in Section 13), undue precision and authority should not be drawn from the category scheme.

Note also that the biological rating system refers only to toxicity which is the ability to cause harm after reaching the target organ or organism. The more important factor upon which to base policy and administrative decisions is related to the <a href="hazard">hazard</a> to health that a chemical poses. Hazard is an expression of the probability that a

chemical will reach the target organ or organism in sufficient quantity to cause harm. Hazard must take into account such factors as the spatial and temporal relationships between the emissions, and the receptor, transport factors, numbers of receptors, etc.

Of the three letters used for ranking, A represents the highest toxicity and C the lowest.

#### Methyl Chloride

Central nervous system depressant. No chronic effects reported at occupational exposure limit levels of 100 ppm (TWA) but no systematic studies reported. Mutagenic in the Ames Test. No reports of carcinogenicity in man or animals, but no long term tests conducted.

Toxicity Rating: [B]

#### Toxicity to Animals

Test Rating

Acute Moderate

Chronic Moderate

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological No Data

#### Methylene Chloride

Central nervous system depressant. Metabolism of compound leads to the formation of carbon monoxide which results in exposure to methylene chloride and carbon monoxide being additive. Occupational exposure level based on keeping CO level within acceptable limits.



Effect unlikely to be important at ambient CO levels.

Additive effect with CO becomes significant at 75 ppm methylene chloride and 10 ppm CO.

Toxicity Rating: [C]

Toxicity to Animals

Test

Rating

Acute

Low

Chronic

Low

Toxicity to Man

Test

Rating

Experimental

Moderate

Epidemiological

Moderate

#### Chloroform

Irritant to eyes, nose and throat. Central nervous system depressant. Liver damage reported after 1-4 years of exposure to 2-205 ppm range. Lassitude reported at 23-35 ppm for 4 hours per day. Fetal abnormallities in rats reported at 30 ppm. At one half maximum tolerated dose, chloroform causes liver cancer in rats. Occupational limit 10 ppm.

Carcinogen at high levels in rats. Liver damage in humans.

Toxicity Rating:

[A]

Toxicity to Animals

Test

Rating

Acute

Moderate

Chronic

High

## Toxicity to Man

<u>Test</u> <u>Rating</u>

Experimental No Data

Epidemiological High

#### Carbon Tetrachloride

Central nervous system depressant. Liver damage in man at around 10 ppm. Restriction of visual fields in man at about 5 ppm. At levels causing severe liver damage, liver cancer found in rats, mice and hamsters. No clear evidence of mutagenicity. Occupational level 2 ppm (TWA). Odor threshold 20-100 ppm.

Carcinogen in rats; causes visual and liver damage in man at low levels.

Toxicity Rating: [A]

Toxicity to Animals

Test Rating

Acute Moderate

Chronic High

Toxicity to Man

Test Rating

Experimental

Epidemiological High

#### 1,2- Dichloroethane

Central nervous system depressant with wide spread harmful effects on clotting of blood. Liver damage and renal effects. Ethylene dichloride is a mutagen in bacterial tests. Occupational exposure level

currently set at 5 ppm (TWA).

Mechanism of toxicity not well understood, but wide variety of organs and organ systems involved at low exposure levels. Not a proven human carcinogen but under suspicion. Carcinogenic to mice and rats.

Toxicity Rating: [A]

## Toxicity to Animals

Test Rating

Acute High

Chronic High

## Toxicity to Man

Test Rating

Experimental No Data

Epidemiological High

## 1,1,1-Trichloroethane

Eye and nose irritant. Central nervous system depressant.

Respiratory tract irritant, because of irritation, occupational exposure limit is a "ceiling" limit of 350 ppm. Little evidence of chronic damage to humans or animals at level below 1000 ppm. Central nervous system depression with giddiness and unsteadyness, prominent between 500-1000 ppm. Irritation of respiratory tract effectively determines exposure limit. Effects reversible below 1000 ppm.

Toxicity Rating: [C]

## Toxicity to Animals

Test Rating

Acute Low

Chronic Moderate

## Toxicity to Man

<u>Test</u> <u>Rating</u>

Experimental Moderate

Epidemiological Moderate

#### 1,1,2,2-Tetrachloroethane

A strong central nervous system depressant with persistent neurological symptoms often reported after end of exposure with tremor of hands and vertigo. Liver damage and jaundice in humans and animals is also prominent feature and occurs at low levels 2-200 ppm.

Occupational exposure limit 1 ppm (TWA).

Toxicity Rating: [A]

#### Toxicity to Animals

Test Rating

Acute High

Chronic High

#### Toxicity to Man

Test Rating

Experimental High

Epidemiological High

## Vinylidene Chloride

An irritant to mucus membranes with its main impact on the liver.

Intermittant exposure of rats (6 hrs/day, 5 days/week for 18 months)

showed minimal changes in the liver at 25-75 parts per million.

Continuous 90 day exposure at 15-5 parts per million produced appreciable mortality among rats, guinea pigs and monkeys. Vinylidene chloride is mutagenic in bacteria. Kidney carcinomata have been reported in male

mice at 25 parts per million vinylidene chloride for 1 year but no such tumors were found in male or female mice exposed at 10 parts per million for one year.

## Toxicity Rating: [B]

No satisfactory human exposure data available upon which an assessement of the hazard of vinylidene chloride to human health could be made.

## Toxicity to Animals

<u>Test</u> <u>Rating</u>

Acute Moderate

Chronic High

Toxicity to Man

<u>Test</u> Rating

Experimental No Data

Epidemiological No Data

#### Trichloroethylene

Eye and nose irritant. Central nervous system depressant. Cancer of the liver produced in rats given very high levels of compound. No cases of cancer due to compound have been reported in man but no detailed epidemiological surveys have been made. Sudden deaths have been reported in workers exposed to "high" levels when undertaking sudden of heavy physical exertion. This effect is thought to be due to cardiac arrhythmias.

Not a proven carcinogen for man. No change has yet been made in occupational limit of 100 ppm (TWA).



Toxicity Rating:

[B]

Toxicity to Animals

Test

Rating

Acute

Low

Chronic

Low

Toxicity to Man

Test

Rating

Experimental

Low

Epidemiological

Moderate

#### Tetrachloroethylene

Central nervous system depressant. No chronic effects in man, rats, monkeys and guinea pigs have been reported below 400 ppm.

Mild reversible, central nervous system depression is reported at levels down to 100 ppm. Present occupational limit is 50 ppm TWA with "Ceiling" value at 100.

Note that Trichloroethylene is very similar to Tetrachloroethylene in toxicity; difference in rating based solely on evidence of cancer in rats at high levels of TCE.

Toxicity Rating:

[C]

Toxicity to Animals

Test

Rating

Acute

Low

Chronic

Low

Toxicity to Man

Test

Rating

Experimental

Low

Epidemiological

Low



## Toxicity to Man

Test	Rating	
Experimental	No Data	
Epidemiological	Moderate	

#### Standards

In Ontario the <u>occupational standards</u> for the chlorinated hydrocarbons of interest here are based on eight hour average concentrations and are usually the same as the TLVs recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Current Standards are listed as:

- methyl chloride	100 (210) ppm (mg.m-3)
- methylene chloride	200 (720)
- chloroform	25 (120)
- carbon tetrachloride	10 (65)
- l,l,l-trichloroethane	350 (1900)
- l,l-dichloroethylene	10 (40)
- trichloroethylene	100 (535)
- tetrachloroethylene	100 (670)
- chloroprene	25 (90)
- chlorobenzene	75 (350)
- p-dichlorobenzene	75 (450)

Ambient air standards in Ontario refer to half hour average point of impingement concentrations. Those compounds of concern here which have been promulgated are:

methylene chloride	$100 \text{ mg.m}^{-3}$
carbon tetrachloride	20

l,l,l-trichloroethane		350
trichloroethylene	Ü	85
l,l-dichloroethylene		26

Water quality standards are generally not compound specific and are regulated by such parameters as BOD, COD, TOC, turbidity, etc.

The exception is drinking water in the U.S. which has a maximum concentration standard for trihalomethanes (including chloroform) of 0.10 mg/l or 100 parts per billion. The USSR also lists standards for a number of compounds in drinking water.

#### Chloroprene

Chloroprene causes central nervous system depression with damage to lungs, liver, and kidneys in rats. Chloroprene has an effect on the developing fetus. Russian epidemiological studies have shown a dose related increase in the incidence of lung and skin cancer in chloroprene workers, changes in spermatogenesis, chromosomes and an increase in abortions were also reported in the two Russian references. The concentrations of chloroprene associated with these changes were from 1 to 7 mg/m $^3$  (3.5 - 24 ppm). If these results are confirmed a downward revision of the present 25 ppm TWA occupational limit can be expected. Carcinogen in man.

Toxicity Rating: [A]

## Toxicity to Animals

Test Rating

Acute High

Chronic High

#### Toxicity to Man

Test Rating
Experimental

Epidemiological High

#### Monoch lorobenzene

Irritant to eyes, skin and upper respiratory tract. Central nervous system depressant. Causes damage to liver, lungs and kidney.

Occupational exposure limit 75 ppm (TWA). No evidence of carcinogenicity but has not undergone adequate testing.

Toxicity Rating:

[c]

Toxicity to Animals

Test

Rating

Acute

Low

Chronic

Moderate

Toxicity to Man

Test

Rating

Experimental

No Data

Epidemiological

Moderate

#### Dichlorobenzene

Ortho Dichlorobenzene is more toxic than para dichlorobenzene.

Both are irritant to eyes and nose and produce liver damage and depression of white cell count in animals. Metabolism to arene oxide raises possibility of carcinogensis but no adequate animal testing has been done to prove whether dichlorobenzene is carcinogenic in animals.

No evidence for carcinogenesis in man. High exposure in man (moth repellents, deodorizers) has resulted in nausea, weakness and jaundice.

Very little dose - response information available. Because of metabolism and reports of effects on blood these compounds should be treated with suspicion as possibly proving to be more toxic than presently considered. Occupational limit, o-dichlorobenzene 50 ppm, p-dichlorobenzene 75 ppm.

Toxicity Rating:

[B]

Toxicity to Animals

Test

Rating

Acute

Moderate

Chronic

Moderate

5 CONTRACTOR'S WORK PROGRAM

# 5 CONTRACTOR'S WORK PROGRAM

An exact copy of the contractor's work program which sets the scope for the study leading to this report and its companion report entitled "Environmental Aspects of Selected Aromatic Hydrocarbons in Ontario:

A Comprehensive Background Report" is reproduced on the following pages.

During the execution of the study a few, relatively minor changes in the work program were agreed upon between UNITED TECHNOLOGY and SCIENCE INC. and the Ministry project officer. These changes are reflected in the content of the reports.

Recommendations arising from this study are contained in a separate report to the Ministry of the Environment.

## Contractor's Work Programme

The Contractor will undertake to provide the Ministry of the Environment with two(2) comprehensive reports- one report each for selected chlorinated hydrocarbons, and for selected aromatic hydro-These in-depth reports are to cover all aspects which are relevant to the role of these compounds as environmental pollutants in Ontario. Each report should represent a state-of-the-art summary and review of up-to-date scientific, technical and medical inform-The information will be obtained by means of literature searches and from a reading of current literature, and be supplemented as required by discussions with knowledgeable professional staff in the university, government and industrial communities. mation and data must be as current as reasonable access to scientific governmental, and industrial sources allows, and should be the most reliable information that is available. Although the Contractor is not expected to reconcile conflicting data, he should endeavour to provide some evaluation and synthesis of the collected information. The Contractor is not expected to generate new laboratory data, or engage in environmental surveys or source testing programmes.

These comprehensive reports should be prepared in sufficient detail to serve as a basis for Ministry policy determination and abatement program design, and otherwise sound decision-making on future Ministry activities.

The study will start with a specification by the Ministry of the Environment of a group of substances which belong to the

chlorinated hydrocarbon and aromatic hydrocarbon classes of chemicals. A preliminary list of compounds is as follows:

### Chlorinated Hydrocarbons:

- Ethylene Dichloride
- Carbon Tetrachloride
- Vinylidine Chloride
- Tetrachloroethylene
- Methyl Chloride
- Chloroprene
- Chloroform
- Methylene Chloride
- Dichloroethylene
- Trichloroethylene
- Trichloroethane

#### Aromatic Hydrocarbons:

- Benzene
- Toluene
- Xylenes
- Naphthalene
- Cumene
- Styrene
- Ethyl Benzene

The study will be carried out in two stages.

## Stage l

The Contractor will carry out activities to identify
the potential sources of environmental emissions for each compound contained in the list specified by the Ministry. Specifically
the Contractor and the final report must give consideration to the
following points:

## Potential Sources of Environmental Emissions

- (a) Types of industries in Ontario which use or produce the specified compounds. Identification of processes and products.
- (b) Estimates of total quantities used or produced in Ontario. Quantities to be subdivided into categories by industrial products, applications, etc.



- (c) Description of major industrial operations and processes which are potential sources. Identification of sources of emissions and types of pollutants.
- (d) Description of potential secondary emitters such as incinerators, non-industrial sources, and ubiquitous sources.
- (e) Estimates of potential environmental emissions or discharges specific to Ontario industries, derived from a knowledge of the industrial operations, control equipment in use, and/or published values of source strengths or emission factors.
- (f) Assessment of the population size potentially exposed to the specified compounds, to be carried out by means of product application assessments and the location of major emitters.

The data collected on industrial sources together with preliminary information on specific health hazards of these compounds will be used in a priority determination to select the compounds for the more intensive information gathering of Stage 2 of this study. This selection will be carried out in consultation with Ministry staff. It is expected that most of the compounds presented above will be considered in Stage 2 since this list already reflects assessments of priority compounds by Ministry staff.

The Contractor will prepare a written progress report at the conclusion of Stage 1 of this study. This progress report is to be in sufficient detail that Ministry staff will be able to identify the major industries, processes, and operations, which use or produce the specified compounds, and which may be potential sources of environmental emissions.

## Stage 2

The high priority compounds selected at the conclusion of Stage 1 will be investigated in great detail using the information sources outlined above. Each comprehensive report must give consideration to the following areas:

## 1. Health Effects:

- (a) Toxicity of specific compounds and dose-response relationships (occupational, environmental).
- (b) Documentation of effects on humans. Source of information (epidemiological surveys, occupational exposure etc.). Special attention should be paid to carcinogenic effects and chronic effects at low dose and extended exposure times.
- (c) Documented instances of community exposure. Population of Ontario potentially affected by specific sources.
- (d) Documentation of effects on animals. Type of test.

  Dose-response relationships for specific compounds.

# 2. Process and Control Technology for Reducing Discharges:

- (a) Description and evaluation of available control apparatus.

  Apparatus appropriate for use by Ontario industries.
- (b) Identification of necessary research and development for improved control and abatement technology.
- (c) 'Identification of need for data from source discharge monitoring and recommendations for specific programmes.

# 3. Persistence and Fate of the Pollutant in the Environment

(a) Decomposition of pollutants in the environment. Other modifications. Characteristics (physical, chemical,



- toxicological) after modification.
- (b) Residence time. Disperal characteristics. Principal removal mechanisms.
- (c) Effect of other substances simultaneously present.
  Reaction rates.

## 4. Sampling and Analytical Techniques:

- (a) Description and evaluation of available apparatus and techniques for various parameters (concentrations, particulate size distribution, chemical composition, etc.). Discussion should be compound - specific if necessary.
- (b) Accuracy, sensitivity, and detection limits of available apparatus and techniques. Adequacy of techniques. Identification of research and development needs. Recommendations.
- (c) Apparatus and techniques currently used by Ontario and other major air pollution agencies.

## 5. Environmental Concentrations:

- (a) Published values of concentrations for specific sources (occupational, ambient environment). Environmental pollution "episodes".
- (b) . Environmental concentrations specific to Ontario industries.
- (c) Need for monitoring of concentrations in vicinity of industrial sources and recommendations for specific programmes.

## 6. Other Effects:

(a) Description of soiling and corrosion effects. Critical



environmental concentrations and conditions (humidity).
Materials affected. Exposure times.

(b) Description of odours. Intensity of odour. Recognition threshold for odours (type of test).

## 7. Standards and Criteria:

(a) Environmental, point of impingement, and occupational standards and criteria in Ontario and elsewhere. Evaluation.

## 8. Chemical and Physical Properties of Pollutants:

Discussions must be compound-specific.

## 9. Recommendations:

Recommendations for further action will include:

- (a) Special surveys in ambient air and water environments ceneral.
- (b) Special surveys in the vicinity of major sources.
- (c) Emission inventories including source testing programs.
- (d) Epidemilogical studies.
- (e) Instrumentation development.

Other relevant topics should not be excluded. Also, the points outlined for each of the above topics are intended only as guides and should not be regarded as restrictive. The Contractor should endeavour to treat each topic as comprehensively as possible. Topics 1,2,3,4,5,9 should be assigned to the highest priority.

6 INTRODUCTION

## 6 INTRODUCTION

The "Hazardous Substances Programme" (HASP) was initiated within the Air Resources Branch of the Ontario Ministry of the Environment in 1974. Among the objectives of the program is the creation of a comprehensive information base on selected substances which have been identified as potentially hazardous in Ontario. This would serve as a component for sound rational decision making in future Ministry activities. To date, separate reports have been issued under HASP dealing with asbestos, and vinyl chloride monomer. This report deals with a number of light chlorinated hydrocarbons:

- methyl chloride
- methylene chloride
- chloroform
- carbon tetrachloride
- dichloroethane
- trichloroethane
- tetrachloroethane
- dichloroethylene
- trichloroethylene
- perchloroethylene
- chloroprene
- chlorobenzene
- dichlorobenzene



The report is divided into a number of key areas in which a thorough review is considered essential in order to derive a reasonable hazard assessment. These include:

- chemical and physical properties
- producers, uses and market forecasts
- process descriptions
- emission and discharge control technology
- sampling and analysis
- environmental persistence and fate
- health effects
- standards

Not included in an overall hazard assessment, but required for the rational development of regulations, are such considerations as alternatives analysis, socioeconomic effects and regulatory options, etc.

This report represents a state-of-the-art review of those key areas listed above with the qualification that only publicly available information was included. No proprietary or confidential information was sought or included.

In order to obtain the information needed, a number of sources were used. These include:

- computer data bases
- scientific and trade journals
- technical manuals and books
- various library holdings

- government publications and reports of government sponsored research
- industrial associations
- leading scientists at universities and other research institutes
- government officials

UNITED TECHNOLOGY and SCIENCE is established as a center for the computer data base searching systems:

- System Development Corporation (ORBIT)
- National Research Council (CAN/OLE)
- National Library of Medicine (MEDLINE)

This allows access to over 50 different data bases. Those bases searched and found to be of most use include:

- Biosis Previews
- Chemical Abstracts Condensates
- Chemical Industry Notes
- Enviroline
- Federal Register
- National Technical Information Service
- Pollution Abstracts
- Toxline

A number of search strategies were composed and used to scan the various data bases for citations. A total of more than 3,000 citations were drawn. Of these, more than 300 were selected and obtained in full text for a detailed study. In addition to these publications, a number of key scientific journals, trade magazines, technical manuals and books were



manually searched for any articles which may have been missed in the computer literature searches. Libraries used include public (Toronto Reference), Universities (University of Toronto, York University, University of Waterloo, and Ryerson College), and government (Ministry of Labor, Ministry of Health, Ministry of the Environment, Atmospheric Environment Service, Environmental Protection Service - Ontario Region and Statistics Canada).

Government publications and publications of work sponsored by government agencies were obtained from the Department of Industry, Trade and Commerce, Statistics Canada, Department of Fisheries and Environment; Ministry of the Environment, Ministry of Health and Ministry of Labor; and the U.S. EPA. Leading scientists in research institutes and government personnel were visited or telephoned to obtain information on current priorities and as yet unpublished studies.

Trade associations such as the Canadian Chemical Producers Association, Canadian Manufacturers of Chemical Specialties, and The Petroleum Association for the Conservation of the Canadian Environment, were contacted with requests for information in addition to a few specific companies. A form letter requesting information on control equipment for industrial emissions/discharges was sent to over 100 manufacturers and distributors.

All suitable information obtained from the above sources was included in the report.

Each major section of the report was written in such a manner that it is more or less independent of the other sections. Therefore, each is

referenced separately. In some sections each compound is considered separately while in others it was considered more suitable to discuss the compounds together.

The Appendix (Section 15) contains a copy of the original (Contractor's Work Programme". During the execution of the study a few, relatively minor, changes in the work program were agreed upon between UNITED TECHNOLOGY and SCIENCE and the Ministry project officer. These changes are reflected in the contents of the report.

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#### 7.1 SUMMARY

The physical and chemical properties of selected chlorinated hydrocarbons are summarized and discussed.

Because of the large diversity of reactions undergone by these compounds, an attempt has been made to limit discussion to those reactions of importance from a technological viewpoint. Thus, degradation reactions, reactions where the compound is or may be used as an industrial intermediate, and reactions of importance in chemical analysis or purification are primarily described.

Reactions of the chlorinated aliphatic hydrocarbons are primarily nucleophilic substitution, elimination, exchange, and addition across the double bond of chlorinated ethylenes.

The important reactions of chlorinated benzenes are electrophilic substitution reactions. However, the degree of chlorination effects the ease with which a particular chlorinated benzene will undergo substitution. This is because a chlorine atom substituted on a benzene ring deactivates the ring towards further substitution. Increasing ring chlorination further deactivates the ring to substitution. Thus the dichlorobenzenes are less reactive towards substitution than chlorobenzene.

Physical properties generally change progressively with increasing degree of chlorination for the chlorinated aliphatic hydrocarbons. Thus, these compounds generally show an increase in density and viscosity with increasing chlorine content, whereas specific heat, dielectric constant and water solubility show a progressive decrease. Exceptions to these

trends occur. Chlorinated benzenes have a more complex relationship between chlorine content and physical properties.

## 7.2 INTRODUCTION

All chlorinated hydrocarbons decompose by oxidation, hydrolysis, or pyrolysis. Oxidation by atmospheric oxygen (autooxidation) is a reaction to which chlorinated olefins are particularly susceptible. This is a chain reaction which may, however, be readily inhibited by the addition of small amounts of organic amines. Nonetheless, chlorinated hydrocarbons are sufficiently stable, thermally and photochemically, to allow their technological use over a wide range of conditions.

Introduction of varying amounts of chlorine into a small number of simple hydrocarbons, such as methane, ethylene, and benzene, yields a wide variety of liquids and solids whose properties can be generally graded according to their degree of chlorination. In general, the physical properties of the chlorinated hydrocarbons change progressively with increase in the number of chlorine atoms substituted into the methane, ethane, and ethylene molecule. Thus, the chlorinated derivatives of these simple aliphatic hydrocarbons show a progressive increase in density and viscosity with increasing chlorine content, while the properties of specific heat, dielectric constant and solubility in water show a corresponding progressive decrease. Several exceptions to these general trends exist, however, eg chloroform is more water-soluble than either methyl chloride or methylene chloride. Chlorinated benzenes show more complex relationships between chlorine content and properties.

The major properties of technological interest introduced to the hydrocambons by chlorination are solvation power, viscosity, reduced flammability and chemical reactivity.

Chlorinated aliphatic hydrocarbons normally undergo nucleophilic substitution reactions, elimination reactions and exchange reactions.

An example of a nucleophilic substitution is the reaction of methyl chloride with a tertiary amine to yield a quaternary ammonium compound; an example of an elimination reaction is the dehydrochlorination of 1,2-dichloroethane to yield vinyl chloride; and an example of an exchange reaction is the exchange of chlorine atoms in carbon tetrachloride with fluorine atoms from antimony trifluoride to yield chlorofluoromethanes.

Chlorinated benzenes generally undergo the same types of reactions as nonchlorinated aromatic hydrocarbons, but require more vigorous conditions because of the deactivating effect towards further substitution of the chlorine substituents on the aromatic nucleus.

The detailed chemical and physical properties outlined in the following sections for each compound are important in assessing the existing or new processes and/or control technologies in use and to properly assess alternative technologies. Those chemical and physical properties which are important in considering the environmental fate and persistence of the compounds of interest in the ambient environment are discussed in greater detail in Section 12.

#### 7.3 METHYL CHLORIDE

#### 7.3.1 INTRODUCTION

Methyl chloride, CH<sub>3</sub>Cl, at ambient temperature and pressure, is a colorless gas with an ethereal odor and a sweetish taste. Commercially, methyl chloride is handled in the liquified form. The liquid is miscible with the principal organic solvents and is only slightly soluble in water. The liquid is stable and noncorrosive when dry; in the presence of moisture it slowly decomposes, becoming corrosive to metals, particularly magnesium, zinc and aluminum. The vapor is moderately flammable, and can produce severe toxic effects on prolonged exposure to high concentrations.

Methyl chloride is used mainly in the manufacture of silicones, tetramethyllead, synthetic rubber, methyl cellulose, and as a methylating agent generally.

Impure methyl chloride was prepared as early as 1835 by Dumas and Peligot, who heated wood spirit (crude methanol) with a mixture of sulfuric acid and common salt. It was later prepared by Schiff and by Walker and Johnson by reacting phosphorus chlorides with methanol. One of the first preparations of pure methyl chloride was by Groves in 1874. Groves passed hydrogen chloride into a boiling solution of zinc chloride in twice its weight of wood spirit. Berthelot obtained the compound by chlorinating methane.

#### 7.3.2 PHYSICAL PROPERTIES

The physical properties of methyl chloride are listed in Table 7-1.

TABLE 7-1

## PHYSICAL PROPERTIES OF METHYL CHLORIDE

Molecular Formula	сн <sub>3</sub> с1
Physical State	gas
Molecular Weight	50.4
Melting Point, °C	-97.7
Boiling Point, °C 101.3 kPa 13.3 kPa 1.3 kPa	-23.73 -61.70 -92.10
Density, liquid, g/cm <sup>3</sup> (20 °C) gas, 0 °C, 101.3 kPa (air = 1)	0.920 1.74
Weight of 1 l of gas, sea level, 45° latitude, 0°C 101.3 kPa, g	2.3045
Refractive Index, n liquid, -23.7 °CD gas, 25 °C	1.3712
Surface tension, mN/m 0 °C 10 °C 20 °C	19.5 17.8 16.2
Specific Heat, liquid, J/g 20 °C -15 → +30 °C (av.)	1.60
Critical Temperature, °C	143.1
Critical Pressure, MPa	6.67
Critical Density, g/cm <sup>3</sup>	0.353
Critical Volume, cm <sup>3</sup> /g	2.833



# TABLE 7-1 (cont.)

Thermal Conductivity, W/m.°C liquid, 20 °C gas, bp	0.168 0.00878
Autoignition Temperature, °C	632
Explosive limits in air, % by vol.	8.1 - 17.2
Combustion Velocity, cm/sec	10.9
Diffusivity in air, 25 °C, 101.3 kPa, cm <sup>2</sup> /sec	0.105
Coefficient of Cubical Expansion, liquid, -30 to 30 °C (av)	0.00209
Dielectric Constant liquid, -25 °C gas, 21 °C	12.93 1.0109
Dipole Moment, esu	$1.86 \times 10^{-18}$
Heat of Formation, ideal gas, 25 °C, kJ/mol	-81.92
Free Energy of Formation, ideal gas, 25 °C, kJ/mol	-58.41
Latent Heat of Fusion, J/g	129.7
Latent Heat of Evaporation, J/g	428.4
Solubility of methyl chloride in water, 25 °C, g/100 g $^{\rm H}2^{\rm O}$	0.48
Solubility of water in methyl chloride, 25 °C, g/100 g methyl chloride	0.0725
Solubility of methyl chloride gas, 20 °C, 101.3 kPa, cm <sup>3</sup> /100 cm <sup>3</sup> solvent benzene carbon tetrachloride glacial acetic acid absolute alcohol	4723 3756 3679 3740

## TABLE 7-1 (cont.)

C.A.S. Registry Number

Synonyms

74-87-3

Chloromethane Artic Freon 40 Values for vapor pressure, specific volume of vapor, and enthalpy of formation of liquid methyl chloride are given in Table 7-2. Table 7-3 lists the values for viscosity of methyl chloride.

#### 7.3.3 CHEMICAL PROPERTIES

Methyl chloride is the simplest chlorinated hydrocarbon. Methyl chloride is the most thermally stable of the chloroparaffin series; when dry, and in the absence of air, it does not decompose appreciably at temperatures approaching 400 °C, even in contact with many metals.

Thermal dissociation of methyl chloride is virtually complete at 1400 °C.

#### 7.3.3.1 DEGRADATION REACTIONS

If methyl chloride liquid is heated in the presence of moisture, slow hydrolysis to methanol and hydrogen chloride occurs below 100 °C.

Oxidative breakdown of the gas requires temperatures of several hundred degrees. In contact with a flame, methyl chloride burns with a white, green-edged flame, the combustion products being principally carbon dioxide and hydrogen chloride. Combustion occurs by a chain reaction, inhibited by the chlorine of the methyl chloride.

When passed over reduced nickel in the presence of excess hydrogen at 210  $^{\circ}$ C, methyl chloride is decomposed to form hydrogen chloride, carbon and hydrogen. It is reduced to methane by heating with calcium carbide at 180  $^{\circ}$ C.

#### 7.3.3.2 HYDROLYSIS REACTIONS

Prolonged exposure to water at elevated temperature results in the

VAPOR PRESSURE, SPECIFIC VOLUME OF VAPOR, AND ENTHALPY OF LIQUID METHYL CHLORIDE

TEMP., °C	VAPOR PRESSURE kPa	SPECIFIC VOLUME OF VAPOR, cm <sup>3</sup> /g	LIQ.	ENTHALPY, kJ VAPORIZATION	VAP.
-20	80.95	499.42	-20.03 -18.12	196.5 195.4	176.5 177.2
-10	103.35	403.28	-16.22 -14.32	194.2 193.1	178.0 178.7
0	129.53	323.38	-12.39 -10.47	191.9 190.6	179.5 180.2
10	160.53	260.95	- 8.50 - 6.58	189.4 188.2	180.9 181.6
20	198.42	212.88	- 4.55 - 2.61	186.9 185.7	182.3 183.0
30	242.25	175.42	- 0.65 1.32	184.4 183.1	183.8 184.4
40	293.50	144.21	3.32 5.31 7.25 9.28	181.8 180.5 179.1 177.8	185.1 185.8 186.4 187.0
60	424.40	100.51	11.28 13.32 15.31 17.35	176.4 175.0 173.5 172.2	187.7 188.3 188.9 189.5
80	587.69	71.17	19.36 21.36 23.33 25.38	170.7 169.2 167.7 166.3	190.0 190.5 191.0 191.7
100	818.5	53.06	27.48	164.8	192.2
110	948.0	47.76	31.66	161.7	193.5

TABLE 7-3

## VISCOSITY OF METHYL CHLORIDE

TEMPERATURE, °C	VISCOSITY	VISCOSITY, mPa.s	
TEMPERATURE,	VAPOR	LIQUID	
-40.0	0.0086	0.349	
-17.8	0.0094	0.298	
4.4	0.0101	0.263	
26.7	0.0108	0.237	
48.9	0.0115	0.217	
71.1	0.0122	0.200	
93.3	0.0128	0.186	
115.6	0.0134	0.175	

hydrolysis of methyl chloride to methanol and hydrochloric acid.

$$CH_3C1 + H_2O \rightarrow CH_3OH + HC1$$

At low temperatures, a solution of methyl chloride in water forms a crystalline hydrate,  $\text{CH}_3\text{Cl.6H}_2\text{O}$ . The hydrate decomposes at 7.5 °C and 101.3 kPa. At 120 °C and 516.7 kPa, methyl chloride saturated with water decomposes at a rate of about 1 g per 100 cm<sup>3</sup> water per hour. This hydrolysis is promoted by the presence of alkali but is unaffected by acid.

#### 7.3.3.3 REACTIONS WITH METALS

Dry methyl chloride reacts with the alkali and alkaline earth metals, magnesium, zinc and aluminium. It is unreactive with all other common metals.

In dry ether solution, methyl chloride reacts with sodium to yield ethane by the Wurtz paraffin synthesis.

$$\text{CH}_3^{\text{Cl}} + 2\text{Na} + \text{ClCH}_3 \rightarrow \text{CH}_3^{\text{CH}}_3 + 2\text{NaCl}$$
 By the same reaction, methyl chloride can react with higher chloroparaffins to give propane and butane, etc.

] ] ]

With sodium in solution in liquified ammonia, methyl chloride reacts to form methane, methylamine, and sodium chloride. On reaction with sodium-potassium alloy, methyl chloride gives methylsodium or methylpotassium as the principal product.

In the manufacture of tetramethyllead,  $Pb(CH_3)_4$ , methyl chloride is reacted with a lead-sodium alloy of appropriate composition.

Magnesium reacts readily with methyl chloride to form a Grignard

reagent, CH<sub>3</sub>MgCl, which is used in the synthesis of alcohols and silicones. The reaction with zinc is similar to that with magnesium.

Methyl chloride in a dry atmosphere has been found not to attack aluminium or its alloys at temperatures up to 60 °C, but in a damp atmosphere, the aluminium alloys, particularly those containing magnesium, are attacked. Reaction with aluminium, when catalyzed by aluminium chloride, can take place with explosive violence (1).

#### 7.3.3.4 REACTIONS WITH HALOGENS AND HALIDES

Methyl chloride is readily converted to the corresponding bromide or iodide by reaction in hot acetone solution with the appropriate sodium halide.

On chlorination with elementary chlorine, methyl chloride is progressively converted to methylene chloride, chloroform, and carbon tetrachloride, a mixture of these chloro-derivatives always being present at any stage.

Bromination can also be achieved by reaction with Br<sub>2</sub>. On heating gaseous methyl chloride with bromine vapor at 300 °C for a contact time of 13 sec., bromochloromethane is the principal product. By passing bromine and methyl chloride at elevated temperature through a reactor packed with charcoal, the chlorine is displaced by bromine, and dibromomethane, bromoform and carbon tetrabromide are produced.

When methyl chloride gas is passed over aluminium bromide at elevated temperature, methyl bromide is the chief product.

#### 7.3.3.5 REACTIONS WITH SALTS

Methyl chloride reacts with metallic salts of organic acids to give the corresponding methyl esters.

$$CH_3C1 + Na OOCCH_3$$
  $290-297 °C$   $CH_3OOCCH_3 + NaC1$ 
 $CH_3C1 + C_6H_5CO^-Na^+$   $300-305 °C$   $C_6H_5COCH_3 + NaC1$ 

On reacting methyl chloride with 5N sodium hydrosulfide solution at 70 °C and 1.21 MPa in the presence of excess hydrogen sulfide, methyl thiol (methyl mercaptan) is produced (side reactions are minimized under these conditions). Methyl thiol is an important organic intermediate.

Methyl cellulose is prepared by reacting methyl chloride with sodium cellulose. This is a similar reaction to the production of methyl esters from sodium alcoholates and phenoxides (Williamson synthesis). Reactions of this type are catalyzed by small amounts of sodium or potassium iodide.

In the presence of aluminium chloride, methyl chloride reacts with aromatic compounds to form the corresponding methyl derivatives.

With benzene, the first product is toluene; however, it is not possible to prevent formation of the other methyl benzenes. Depending on the conditions and proportions of reactants, every level of methylation up to hexamethylbenzene may result.

Aluminium chloride catalyses a reaction between methyl chloride and carbon monoxide, forming acetyl chloride.

Highly branched hydrocarbon structures are produced when peroxidefree olefins are methylated with methyl chloride at about 240 °C in the presence of high-calcium lime which has been calcined under carefully controlled conditions.

### 7.3.3.6 REACTION WITH AMMONIA AND AMINES

Methyl chloride reacts with ammonia in alcoholic solution or in the gas phase. The relative amounts of methylamine, trimethylamine, and tetramethyl ammonium chloride formed depends on the conditions of the reaction. Since hydrogen chloride is coproduced with these amines, they are obtained as their hydrochlorides.

 $\text{CH}_3^{\text{Cl}} + \text{NH}_3 \rightarrow \text{CH}_3^{\text{NH}}_2 + \text{HCl} \rightarrow \text{CH}_3^{\text{NH}}_2 \cdot \text{HCl}$  With tertiary amines, methyl chloride forms quaternary derivatives.

$$CH_3C1 + NR_3 \rightarrow [R_3NCH_3]^+C1^-$$

#### 7.4 METHYLENE CHLORIDE

#### 7.4.1 INTRODUCTION

Methylene chloride,  $\mathrm{CH_2Cl_2}$ , is a colorless, heavy, mobile liquid with a pleasant ethereal odor. It is the least toxic of the chloromethanes. Methylene chloride is practically nonflammable, but is capable of forming explosive mixtures with air or oxygen. It is one of the most stable chloroparaffins and shows no appreciable decomposition on contact with water and metals up to its boiling point. The outstanding solvent properties of methylene chloride are the basis of its principal uses in industry.

Methylene chloride was first prepared in 1840 by Regnault by chlorinating methyl chloride in sunlight. The compound was prepared by Perkin in 1868 by reducing chloroform with zinc dust and hydrochloric acid. Butlerow made a thorough investigation of the compound in 1869.

Methylene chloride is principally used in paint stripper formulations.

Other important applications are in solvent degreasing, aerosol propellant manufacture, and the production of photographic film and synthetic fibres.

#### 7.4.2 PHYSICAL PROPERTIES

The physical properties of methylene chloride are listed in Table 7-4 (2). The vapor pressure-temperature relationship for methylene chloride is presented in Table 7-5.

The binary azeotropes formed with methylene chloride are listed in Table 7-6.

TABLE 7-4

### PHYSICAL PROPERTIES OF METHYLENE CHLORIDE

Molecular Formula	<sup>CH</sup> 2 <sup>Cl</sup> 2
Physical State	liquid
Molecular Weight	84.93
Melting Point, °C	-95.1
Boiling Point, °C	40.4
Density, g/cm <sup>3</sup> , (20 <sup>t/c</sup> )	1.4242
Vapor Density (air = 1)	2.93
Refractive Index $n_D^{20}$ , liquid $n_D^{25}$ , vapor	1.3266 1.001055
Surface Tension in Air, mN/m 15 °C 20 °C 30 °C	28.83 28.12 26.54
Viscosity, mPa.s liquid, 15 °C liquid, 20 °C vapor, bp	0.449 0.425 0.0109
Specific Heat, liquid, 15-45 °C, J/g	1.205
Specific Heat, vapor, J/g  C C V	0.675 0.577
Critical Temperature, °C	273
Critical Pressure, MPa	6.08
Molar Volume, 24.7 °C, cm <sup>3</sup> /g	44.46
Ignition Temperature, °C	662

## TABLE 7-4 (cont.)

Explosive Limits in Oxygen, % by vol.	15.5 - 66
Diffusivity in Air, 25 °C, 101.3 kPa, cm <sup>2</sup> /sec	0.091
Evaporation Rate (ether = 100)	71
Coefficient of Cubical Expansion, liquid, 0-40 <sup>6</sup> C	0.00137
Dielectric Constant solid, -190 °C solid, -100 °C liquid, -100 °C liquid, 20 °C liquid, 40 °C	3.0 3.5 16.98 9.1 8.29
Heat of Formation, liquid, 18 °C, kJ/mol	120.6
Heat of Combustion, kJ/mol	604.5
Heat of Combustion of gas to aqueous HCl at constant pressure, kJ/mol	446.9
Free Energy of Formation, liquid, 25 °C, kJ/mol	-106.6
Latent Heat of Fusion, kJ/mol	4.60
Latent Heat of Evaporation, J/g	329.3
Solubility in Water, g/100 g H <sub>2</sub> 0 0 °C 10 °C 20 °C 30 °C	2.36 2.12 2.00 1.97
Solubility of Water in $\mathrm{CH_2Cl_2}$ , 25 °C, $\mathrm{g/100~g~CH_2Cl_2}$	0.170
C.A.S. Registry Number	75-09-2
Synonyms	Dichloromethane Methylene dichloride Freon 30



## TABLE 7-5

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR METHYLENE CHLORIDE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
0	19.64
10	30.60
20	46.48
30	68.13
35	79.93
40.4	101.32

TABLE 7-6

BINARY AZEOTROPES OF METHYLENE CHLORIDE

SECOND COMPONENT	BP OF AZEOTROPE, °C	CH2Cl2, wt. %
Water	38.1	98.5
Methanol	39.2	94.0
Tert-butyl alcohol	57.1	94.0
2-propanol	56.6	92.0
Ethanol	54.6	88.5
lodomethane	39.8	79.0
Propylene Oxide	40.6	77.0
Cyclopentane	38.0	70.0
Ether	40.8	70.0
Acetone	57.6	70.0
Carbon Disulfide	37.0	61.0
Diethylamine	52.0	45.0



Methylene chloride dissolves with difficulty in liquid ammonia at room temperature. It dissolves readily in many phenols, aldehydes, ketones, and in glacial acetic acid, triethyl phosphate, acetoacetic ester, formamide, and cyclohexylamine. Methylene chloride is miscible in all proportions with the commercial chlorinated solvents, ether and ethanol.

Methylene chloride vapor is absorbed by polystyrene film (1).

#### 7.4.3 CHEMICAL PROPERTIES

#### 7.4.3.1 DEGRADATION REACTIONS

Methylene chloride is slightly less stable than methyl chloride.

No pyrolysis of dry methylene chloride vapor takes place up to 290 °C, and there is no reaction with oxygen. If the vapor, mixed with oxygen, is passed over copper oxide at 450 °C, a small quantity of phosgene is formed. On prolonged heating at 140-170 °C with water in a sealed vessel, methylene chloride forms formaldehyde and hydrochloric acid.

$$CH_2C1_2 + H_2O \rightarrow HCHO + 2HC1$$

Prolonged heating with water at 180 °C yields formic acid, methyl chloride, methanol, hydrochloric acid, and some carbon dioxide. Methylene chloride will also form a hydrate.

The decomposition of methylene chloride in contact with air and moisture (conditions found in industry) can be inhibited by the addition of small quantities (0.0001 - 1%) of phenolic compounds, eg phenol, hydroquinone, p-cresol, resorcinol, thymol or l-naphthol (2). Methylene

chloride can also be stabilized by addition of small quantities of amines, or a mixture of nitromethane and 1,4-dioxane.

#### 7.4.3.2 REACTION WITH METALS AND SALTS

Methylene chloride does not react with the common metals when dry and at ambient temperatures, but will react with aluminium and alloys of sodium and potassium. It reacts explosively with sodium. In contact with water, especially at higher temperatures, methylene chloride corrodes iron, some stainless steels, copper, nickel and some other metals and alloys.

Methylene chloride can take part in various Wurtz and Wurtz-Fittig reactions. The Wurtz reaction involves reaction with sodium to form aliphatic hydrocarbons, and the Wurtz-Fittig reaction involves unsymmetrical coupling of alkyl and aryl halides in the presence of sodium to yield alkarylhydrocarbons.

Methylene chloride reacts with anhydrous sodium acetate and ethanol at 170 °C to yield a mixture of diethoxymethylene,  $\text{CH}_2(\text{OC}_2\text{H}_5)_2$ , and acetoacetic ester,  $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$ .

When methylene chloride is heated with aqueous potassium sulfite at 150-160 °C, dipotassium methane disulfonate is produced.

Methylene chloride vapor reacts at 300-400 °C with a mixture of reduced copper and silicon, in a nitrogen atmosphere, to yield a mixture of organosilicon derivatives.

Methylene chloride reacts with carbon monoxide in the presence of aluminium at a temperature of 200  $^{\circ}$ C and a pressure of 91.2 MPa to yield chloroacetylchloride, CH $_{2}$ CICOCI.

Methylene chloride vapor, when contacted with reduced nickel at 200 °C in the presence of excess hydrogen, is reduced to hydrogen chloride and elementary carbon.

In the presence of aluminium chloride, methylene chloride will react with benzene to produce diphenylmethane; with toluene a mixture of p,p'-, and m,p'-ditolyl methanes and three isomeric dimethyl anthracenes is produced. Reaction of methylene chloride with biphenyl using aluminium chloride catalyst yields fluorene.

## 7.4.3.3 REACTIONS WITH AMMONIA AND NITROGEN COMPOUNDS

Methylene chloride is readily reduced to methyl chloride and methane by alkali metal ammonium compounds in liquid ammonia.

When methylene chloride is heated with alcoholic ammonia at 100-125  $^{\circ}$ C, a heterocyclic ring compound, hexamethylenetetramine, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, is formed; with aqueous ammonia at 200  $^{\circ}$ C, hydrogen chloride, formic acid and methylamine are formed.

Methylene chloride vapor reacts with nitrogen dioxide at 270 °C to yield a mixture consisting mainly of carbon monoxide, nitric oxide, and hydrogen chloride.

#### 7.4.3.4 HALOGENATION REACTIONS

Methylene chloride is easily chlorinated to chloroform and carbon tetrachloride in the presence of a chlorination catalyst.

If an excess of a methylene chloride and bromine mixture is reacted with aluminium at 26-30 °C, bromochloromethane is produced. Methylene chloride reacts with iodine at 200 °C to give methylene iodide,  $\text{CH}_2\text{I}_2$ .

The reaction of methylene chloride with bromine iodide, BrI, at l10-180 °C, yields a mixture of methylene iodide, methyl iodide, and chlorodiiodomethane ( $\mathrm{CH_2CII_2}$ ).

When methylene chloride is reacted with iodine and potassium iodide at 180-200 °C, a complex mixture of products is obtained. Among the products are carbon dioxide, potassium chloride, methylene iodide, and ethyl iodide.

#### 7.5 CHLOROFORM

#### 7.5.1 INTRODUCTION

Chloroform, CHCl<sub>3</sub>, is a heavy, colorless, volatile liquid having a pleasant, etheric, nonirritant odor. It is nonflammable, but the hot vapor in admixture with vaporized alcohol burns with a green-tinged flame. Chloroform is miscible with the principal organic solvents and slightly soluble in water.

Chloroform was discovered almost simultaneously in 1831, by Leibig, who obtained it by the action of alkali on chloral, and by Soubeirain who obtained chloroform by reaction of bleaching powder with alcohol or acetone. Guthrie has also been claimed as a third discoverer of chloroform in 1831. In 1839, Dumas produced chloroform by heating trichloroacetic acid with alkali. In 1840, Renault obtained chloroform by chlorination of methyl chloride.

The most important use of chloroform is as the starting material in the manufacture of chlorodifluoromethane, CHClF<sub>2</sub>. Chloroform is also used as an extractant for naturally occurring substances, as a soil fumigant, and as a heat-transfer medium. Use of chloroform for anaesthesia is now rare, but this high-purity grade of chloroform is used in the manufacture of pharmaceutical preparations.

### 7.5.2 PHYSICAL PROPERTIES

The physical properties of chloroform are listed in Table 7-7 (1, 2). The vapor pressure-temperature relationship for chloroform is presented in Table 7-8 (1). Chloroform forms a number of binary azeotropes and these are listed in Table 7-9.

## TABLE 7-7

## PHYSICAL PROPERTIES OF CHLOROFORM

Molecular Formula	CHC13
Physical State, S.T.P.	liquid
Molecular Weight	119.38
Melting Point, °C	-63.5
Boiling Point, 101.3 kPa, °C	61.7
Density, g/cm <sup>3</sup> 0 °C 20 °C 25 °C 60.9 °C	1.5264 1.4832 1.4807 1.4081
Vapor Density, 101.3 kPa, 0 °C, g/l	4.36
Refractive Index, n <sub>D</sub> 12.5 °C 18.5 °C 20 °C 25 °C	1.4506 1.4457 1.4467 1.4422
Surface Tension, mN/m air, 20 °C air, 25 °C air, 60 °C water, 20 °C	27.14 26.5 21.73 45.0
Specific Heat, 20 °C, J/g, °C	0.979
Critical Temperature, °C	263.4
Critical Pressure, MPa	5.45
Critical Density, g/cm <sup>3</sup>	0.5
Critical Volume, cm <sup>3</sup> /g	2.0
Thermal Conductivity, 20 °C, W/m. °C	2.405

## TABLE 7-7 (cont.)

Coefficient of Cubical Expansion	0.001399
Dielectric Constant, 20 °C	4.9
Dipole Moment, esu	$1.15 \times 10^{-18}$
Heat of Combustion, kJ/mol	373.2
Heat of Formation, kJ/mol gas liquid	89.66 120.92
Latent Heat of Evaporation, bp, J/g	246.9
Solubility of chloroform in water, g/100 H <sub>2</sub> 0 0 °C 10 °C 20 °C 30 °C Solubility of water in chloroform, 22 °C,	1.062 0.895 0.822 0.776
g/100 g CHCl	0.0806
Viscosity, liquid, mPa.s -13 °C 0 °C 15 °C 20 °C 30 °C	0.855 0.700 0.596 0.563 0.510
C.A.S. Registry Number	67-66-3
Synonyms	Trichloromethane Freon 20 Trichloroform

TABLE 7-8

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR CHLOROFORM

TEMPERATURE, °C	VAPOR PRESSURE, kPa
-60	0.108
-50	0.274
-40	0.626
-30	1.332
-20	2.611
-10	4.630
0	8.127
10	13.389
20	21.263
30	32.773
40	48.133
50	70.076

TABLE 7-9

## BINARY AZEOTROPES OF CHLOROFORM

SECOND COMPONENT	BP OF AZEOTROPE, °C	CHCl3, wt %
2-but anone	79.7	4.0
2-bromopropane	62.2	65.0
methyl acetate	64.8	77.0
acetone	64.5	79.5
formic acid	59.2	85.0
ethyl formate	62.7	87.0
methanol	53.5	87.5
2-propanol	60.8	95.5
n-hexane	60.0	97.2
water	56.1	97.2

Chloroform forms a ternary azeotrope with ethanol and water which boils at  $55.5~^{\circ}\text{C}$  and contains 4 mole % of ethanol and 3.5 mole % of water.

Chloroform is an excellent solvent and dissolves alkaloids, cellulose acetate and benzoate, ethyl cellulose, essential oils, fats, halogens, methyl methacrylate, mineral oils, many resins, rubber, tars, vegetable oils, and a wide range of common organic compounds. At 25 °C, chloroform dissolves 3.5 times its weight of carbon dioxide.

#### 7.5.3 CHEMICAL PROPERTIES

#### 7.5.3.1 DEGRADATION REACTIONS

Chloroform slowly decomposes on prolonged exposure to sunlight in the presence or absence of air, and in the dark when air is present.

The products of breakdown include phosgene, hydrogen chloride, chlorine, carbon dioxide, and water. When in contact with iron and water, an oxidation product of chloroform is hydrogen peroxide. This is believed produced by the reaction:

Oxidation of chloroform with powerful oxidizing agents, such as chromic acid, produces phosgene and chlorine. Nitrogen dioxide at arount 270 °C oxidizes chloroform to a mixture of compounds, including phosgene, hydrogen chloride, water, and carbon dioxide. Ozone forms a blue solution in chloroform with rapid formation of phosgene, etc.

Chloroform is not appreciably decomposed on prolonged contact with water at ambient temperature in the absence of air. On prolonged heating with water at 225 °C, chloroform is decomposed to formic acid, carbon monoxide and hydrogen chloride.

Chloroform is decomposed at elevated temperature by potassium hydroxide.

$$CHC1_3 + 4KOH \rightarrow HCOOK + 3KC1 + 2H_2O$$

Chloroform does not thermally decompose at temperatures up to 290 °C. Pyrolysis of chloroform takes place at temperatures above 450 °C, the products being tetrachloroethylene, hydrogen chloride, and a number of chlorohydrocarbons as minor components. Pyrolysis of chloroform on hot pumice is catalyzed by vaporized iodine. The main products of this reaction are tetrachloroethylene, hexachloroethane, and carbon tetrachloride.

Chloroform reacts on contact with red-hot copper or with potassium amalgam, to form acetylene.

$$2CHC1_3 + 6K[Hg] \rightarrow CH = CH + 6KC1[Hg]$$

Chloroform is normally stabilized against decomposition in storage by the addition of small quantities of ethanol.

Chloroform can be reduced with zinc dust and aqueous ethanol to methane. If ammonia is present the reduction yields methylene chloride as well as methane.

#### 7.5.3.2 HALOGENATION REACTIONS

Chloroform reacts readily with halogens or halogenating agents.

Chloroform vapor reacts with elemental chlorine upon irradiation, by a free radical chain mechanism.

Bromination of chloroform vapor at 225-275 °C gives bromochloromethanes,  $CC1_3Br$ ,  $CC1_2Br_2$ ,  $CC1Br_3$ . Chloroform is converted to bromoform by reaction with aluminium bromide.

#### 7.5.3.3 OTHER REACTIONS

Chloroform condenses with acetone at about 50 °C to yield chlorobutanol. The presence of an alkali metal hydroxide is required.

Chlorobutanol is a white crystalline compound with an odor similar to camphor: its sedative, anaesthetic and antiseptic properties are of interest in the pharmaceutical industry.

Chloroform in alcoholic alkali solution reacts with aniline and other amines to form isonitriles.

$$CHC1_3 + C_6H_5NH_2 + 3KOH \rightarrow C_6H_5NEC + 3KC1 + 3H_2O$$

Chloroform combines with the anhydride of salicylic acid to form a crystalline compound of the form;

The above complex, on heating, readily liberates chloroform. This reaction has been used to produce high purity chloroform.

#### 7.6 CARBON TETRACHLORIDE

#### 7.6.1 INTRODUCTION

Carbon tetrachloride, CCl<sub>4</sub>, is a heavy, colorless, nonflammable liquid with a characteristic, non-irritant odor. The vapor, in contact with a flame or very hot surface, decomposes to give toxic products, including phosgene. The commercial product normally contains stabilizers.

Carbon tetrachloride was discovered in 1839 by Regnault, who prepared it by chlorinating chloroform. Dumas prepared carbon tetrachloride by chlorinating methane (marsh gas) shortly afterwards. Kolbe produced the compound in 1843 by passing a mixture of carbon disulfide and chlorine through a packed mass of red-hot pieces of porcelain. Liquid phase chlorination of carbon disulfide, the principal process for carbon tetrachloride manufacture until the late 1950's, was developed by Muller and Dubois in 1893 (1).

#### 7.6.2 PHYSICAL PROPERTIES

Table 7-10 lists the physical properties of carbon tetrachloride (1, 2). Tables 7-11 and 7-12 list the viscosity-temperature relationship and vapor pressure-temperature relationship for carbon tetrachloride respectively (1). Carbon tetrachloride forms a number of binary azeotropes, and these are listed in Table 7-13; several ternary azeotropes are also known.

Carbon tetrachloride is miscible with a large number of common organic liquids, and is a powerful solvent for asphalt, benzyl resin (polymerized benzyl chloride), bitumens, chlorinated rubber, ethyl

## <u>TABLE 7-10 (cont.)</u>

Average Coefficient of Volume Expansion, 0-40 °C	0.00124
Dielectric Constant liquid, 20 °C liquid, 50 °C vapor, 87.6 °C	2.25 1.874 1.00302
Heat of Formation, kJ/mol liquid vapor	141.4 108.4
Heat of Combustion, Iqiuid, at constant volume, 18.7 °C, kJ/mol	365.3
Latent Heat of Fusion, kJ/mol	2.54
Latent Heat of Evaporation, bp, J/g	194.8
Solubility of CCl4 in water at 25 °C, g/100 g $\rm H_2^{0}$	0.08
Solubility of water in CCl $_4$ at 25 °C, g/100 g CCl $_4$	0.013
C.A.S. Registry Number	56-23-5
Synonyms	Tetrachloromethane Perchloromethane Carbon chloride Benzinoform Tetraform Necatorina Freon 10

## TABLE 7-11

# VISCOSITY-TEMPERATURE RELATIONSHIP FOR CARBON TETRACHLORIDE

TEMPERATURE, °C	VISCOSITY, mPa.s
0	1.329
20	0.965
30	0.845
40	0.739
50	0.651
60	0.585
70	0.527
80	0.466
90	0.426
100	0.383
180	0.201

TABLE 7-12

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR CARBON TETRACHLORIDE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
-50.1	0.123
-20	1.323
-10	2.508
0	4.410
10	7.419
20	11.94
30	18.61
40	28.12
50	41.20
60	58.53
70	81.83
76.72	101.3
150	607.3
200	1458.0

TABLE 7-13

## AZEOTROPES OF CARBON TETRACHLORIDE

SECOND COMPONENT	BPT OF AZEOTROPE, °C	CC14 % BY WT.
n-butanol	77	97.5
2-methyl-2-butanol	76	95.0
acetic acid	77	97.0
n-propanol	73	88.5
ethyl nitrate	75	84.5
ethanol	65	84.0
nitromethane	71	83.0
iso-propanol	69	82.0
1,2-dichloroethane	76	79.0
tert-butanol	70.5	76.0
methyl propionate	76	75.0
n-propyl formate	75	69.0
acetone	56	11.5

cellulose, fats, gums, rosin, and waxes. It will readily dissolve stannic chloride, SnCl<sub>4</sub>. A number of polymers films, eg polyethylene, polyacrylonitrile, are permeable to carbon tetrachloride vapor.

Carbon tetrachloride vapor affects the explosive limits of a number of gaseous mixtures, eg air-hydrogen and air-methane. Carbon tetrachloride vapor has an extinguishing effect on a flame, mainly because of a cooling action caused by its high thermal capacity.

In carbon tetrachloride, the tetrahedral symmetry of methane, disturbed in the other chloromethanes, is restored. The length of the C-Cl bond along the chloromethane series decreases from 0.1786 nm in methyl chloride to 0.1755 nm in carbon tetrachloride.

#### 7.6.3 CHEMICAL PROPERTIES

#### 7.6.3.1 DEGRADATION REACTIONS

Thermal decomposition of carbon tetrachloride takes place slowly at about 400 °C; between 900 and 1300 °C, dissociation is extensive, forming perchloroethylene and hexachloroethane and liberating some chlorine. The effect of an electric arc on carbon tetrachloride vapor is to form perchloroethylene and hexachloroethane, and in addition, hexachlorobenzene, elementary carbon, and chlorine.

Carbon tetrachloride is the least resistant of the chloromethanes to oxidative breakdown. When mixed with air and heated in the presence of iron at 335 °C, 375 mg of phosgene are produced from 1 g of carbon tetrachloride, compared to only 2.4 mg of phosgene produced from 1 g of chloroform under the same conditions.

When mixed with excess water and heated to 250 °C, carbon tetrachloride decomposes to carbon dioxide and hydrochloric acid; with a limited amount of water, phosgene is formed. This decomposition also occurs when wet carbon tetrachloride is exposed to light (wavelength 253.7 nm) at ambient temperatures. With steam at high temperatures, chloromethanes, hexachloroethane, and perchloroethylene are formed.

#### 7.6.3.2 REACTIONS WITH METALS

Dry carbon tetrachloride has no effect on most commonly used construction metals, eg iron and nickel. However, it reacts slowly with copper and lead. Carbon tetrachloride is reactive, sometimes explosively, with aluminium and its alloys. It is believed that moisture must be present for reaction with aluminium to occur (1).

In contact with metallic sodium or potassium, or a liquid alloy of both metals, carbon tetrachloride forms products which may explode under shock. Carbon tetrachloride is decomposed to sodium chloride and elemental carbon on heating with sodium.

Carbon tetrachloride can be reduced to chloroform by heating with zinc and hydrochloric acid. With potassium amalgam and water, total reduction to methane occurs. The reducibility of carbon tetrachloride has been applied in a patented process to produce perchloroethylene by reaction of chloroethanes and carbon tetrachloride at 400-500 °C in the presence of a catalyst (1).

$$2CHC1_2CHC1_2 + 2CC1_4 \rightarrow 3CC1_2=CC1_2 + 4HC1$$

#### 7.6.3.3 HALOGENATION REACTIONS

Reaction of carbon tetrachloride with aluminium bromide at 100 °C, or with calcium iodide,  $Cal_2$ , at 75 °C produce carbon tetrabromide or tetraiodide respectively. With concentrated hydriodic acid at 130 °C, iodoform,  $CHI_3$ , is produced.

Carbon tetrachloride is unaffected by gaseous fluorine at ambient temperatures; chlorine replacement by fluorine is accomplished by reaction with hydrogen fluoride at 230-300 °C and 5.2-6.9 MPa pressure, yielding dichlorodifluoromethane as the major product. Replacement of more than two chlorine atoms in carbon tetrachloride with fluorine using hydrogen fluoride is difficult, and requires other techniques.

#### 7.6.3.4 OTHER REACTIONS

Carbon tetrachloride forms telomers with ethylene and certain vinyl derivatives. Those derived from ethylene have the general formula,

in which n is an integer from 1 to 8.

Carbon tetrachloride when mixed with water, cooled, and seeded with crystals of chloroform hydrate, forms crystals of a hydrate which decompose at 1.4-1.49 °C (101.3 kPa).

 In the presence of anhydrous aluminium chloride, benzene reacts with carbon tetrachloride to form triphenylchloromethane, no tetraphenylmethane being formed.

At elevated temperatures carbon tetrachloride reacts with silica gel, forming a silicon oxychloride.

#### 7.7 DICHLOROETHANE

#### 7.7.1 INTRODUCTION

There are two isomers of dichloroethane; l,l-dichloroethane (ethylidene chloride),  $\mathrm{CH_3^{CHCl}_2}$ , and l,2-dichloroethane (ethylene dichloride),  $\mathrm{CH_2^{CICH}_2^{Cl}}$ . Both isomers are colorless liquids with odors resembling that of chloroform.

1,2-dichloroethane was the earliest known chlorinated hydrocarbon, having been produced in 1795 by four Dutchmen, Deimann, Van Troostwyk, Bondt, and Louwrenburgh. For many years it was known as "oil of the Dutch chemists".

#### 7.7.2 PHYSICAL PROPERTIES

The physical properties of the two dichloroethane isomers are listed in Table 7-14 (1). The vapor pressure-temperature relationships for the two isomers are presented in Table 7-15.

The solubility of 1,1-dichloroethane in water at 20 °C is 0.55 g/100 g  $\rm H_2^0$ . The solubility of water in 1,1-dichloroethane at 20 °C is 0.009 g/100 g 1,1-dichloroethane. 1,1-dichloroethane forms an azeotrope containing 1.9 %  $\rm H_2^0$  which boils at 53.3 °C at 97.33 kPa; an azeotrope with ethanol contains 8 % ethanol and boils at 54.5 °C.

1,1-dichloroethane is miscible with chlorinated solvents and is soluble in the other common organic solvents. It is itself a solvent for many organic materials and compounds.

The solubility of 1,2-dichloroethane in water at 20 °C is 0.869 g/100 g  $H_2^0$ ; solubility of water in 1,2-dichloroethane at 20 °C is 0.160 g/100 g 1,2-dichloroethane.

TABLE 7-14

PHYSICAL PROPERTIES OF THE DICHLOROETHANE ISOMERS

	1,1-ISOMER	1,2-ISOMER
Molecular Formula	CH3-CHC12	сн <sub>2</sub> с1-сн <sub>2</sub> с1
Physical State	liquid	liquid
Molecular Weight	98.96	98.96
Melting Point, °C	-97.0	-35.4
Boiling Point, °C	57.3	93.5
Density, 20 °C, g/cm <sup>3</sup>	1.1757	1.2351
Refractive Index, n <sub>D</sub> <sup>20</sup>	1.4164	1.4448
Viscosity, mPa.s 15 °C 20 °C 30 °C	0.505 - 0.430	0.887 0.840 0.730
Surface Tension, mN/m 15 °C 20 °C 30 °C	25.32 24.75 23.62	32.93 32.23 30.84
Latent Heat of Fusion, J/g	-	88.37
Latent Heat of Evaporation, bpt, J/g	-	323.4
Specific Heat, J/g, °C liquid, 20 °C vapor, 101.3 kPa, 97.1 °C	-	1.29 1.07
Critical Temperature, °C	250	288
Critical Pressure, MPa	5.07	5.37
Critical Density, g/cm <sup>3</sup>	~	0.44
Flash Point, °C closed cup open cup	-8.5	17 21

## TABLE 7-14 (cont.)

Autoignition Temperature in air, °C	-	449
Explosive limits in air, % by volume	5.9 - 15.9	6.2 - 16.9
Heat of Combustion, kJ/mol  C C P	1118.8 1117.5	1240.0
Thermal Conductivity, W/m. °C	-	1.43
Heat of Formation, kJ/mol liquid vapor	-	157.3 122.6
Dielectric Constant liquid, 20 °C vapor, 120 °C	10.9	10.45 1.00481
Dipole Moment, esu	-	$1.57 \times 10^{-18}$
Steam Distillation Point, 101.3 kPa, °C	-	71.4
Coefficient of Cubical Expansion, av., 0-30 °C	-	0.00117
C.A.S. Registry Number *	75-34-3	107-06-2
Synonyms	Ethylidene chloride	Sym-dichloroethane Ethylene dichloric Glycol dichloride Dutch liquid

<sup>\*</sup> C.A.S. Registry Number for dichloroethane (isomer unspecified) is 1300-21-6

TABLE 7-15

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP

# FOR THE DICHLOROETHANE ISOMERS

TEMPERATURE, °C	VAPOR PRESSURE, kPa	
	1,1-ISOMER	1,2-ISOMER
0	9.35	3.33
10	15.37	5.33
20	24.28	8.53
30	36.96	13.33
40	~	21.33
50	. <del></del>	32.00
60	-	46.66
70	-	66.66
80	=	93.33
83.5	-	101.3

1,2-dichloroethane is reported to form twelve binary azeotropes (1); the one with water contains 8.1~%  $_2^0$  and boils at 71.9~%. A ternary azeotrope, containing 78~% 1,2-dichloroethane, 17~% ethanol, and 5~%  $_2^0$ , is known, which boils at 66.7~%.

l,2-dichloroethane is miscible with all of the chlorinated solvents and is soluble in the other common organic solvents. It is itself a solvent for fats, greases, waxes, and many other organic materials and compounds.

### 7.7.3 CHEMICAL PROPERTIES

When heated to temperatures above 150 °C, in the presence of chlorine and steel wire, 1,1-dichloroethane decomposes to give vinyl chloride and hydrogen chloride.

1,2-dichloroethane is stable at ambient temperature when dry. In the presence of air, moisture, and light, 1,2-dichloroethane at ambient temperature undergoes slow decomposition, becomes acidic, and darkens in color. This decomposition is inhibited in the commercial product by the addition of small amounts (about 0.1 wt %) of alkylamines.

At 600 °C and higher temperatures, 1,2-dichloroethane decomposes to give vinyl chloride, hydrogen chloride, and acetylene.

1,2-dichloroethane is hydrolyzed to ethylene glycol by slightly acidified water at 160-175 °C under a pressure of 1.5 MPa. Hydrolysis to ethylene glycol can also be effected by reaction with aqueous alkali at 140-250 °C under a pressure of 4.1 MPa.

l,l-dichloroethane is converted to acetaldehyde on reaction with warm aqueous alkali solution.

Upon chlorination at 50  $^{\circ}$ C under a mercury vapor lamp, 1,2-dichloro-ethane forms 1,1,2-trichloroethane; further chlorination produces higher chloroethanes.

Both chlorine atoms of the 1,2-dichloroethane molecule are reactive and can be replaced by various functional groups or radicals, eg sodium cyanide reacts to form succinic acid dinitrile, CH<sub>2</sub>CNCH<sub>2</sub>CN, and ammonia reacts at 120 °C under pressure to form ethylenediamine, CH<sub>2</sub>NH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>.

Reaction of 1,2-dichloroethane with sodium polysulfide yields a rubberlike material known as polyethylene tetrasulfide.

In the presence of Friedel-Crafts catalysts, eg AlCl $_3$ , both chlorine atoms of 1,2-dichloroethane react with aromatic hydrocarbons; for example, diphenylethane,  $C_6H_5CH_2CH_2C_6H_5$  is formed on reaction with benzene.

1,2-dichloroethane reacts with oleum to give 2-chloroethylsulfuryl chloride,  $HC_2CICH_2OSO_2CI$ .

#### 7.8 TRICHLOROETHANE

#### 7.8.1 INTRODUCTION

There are two isomers of trichloroethane; 1,1,1-trichloroethane (methyl chloroform),  $\text{CH}_3^{\text{CCl}}_3$ , and 1,1,2-trichloroethane,  $\text{CH}_2^{\text{CICHCl}}_2$ . Both isomers are colorless, nonflammable liquids with characteristic odors.

Both isomers of trichloroethane were among a group of chlorinated hydrocarbons discovered by Regnault in 1839-1840; 1,1,2-trichloroethane was identified by Kramer in 1870 as a by-product of chloral manufacture. The 1,1,2-isomer is more toxic than the 1,1,1-isomer.

#### 7.8.2 PHYSICAL PROPERTIES

The physical properties of the two trichloroethane isomers are listed in Table 7-16 (1, 2). The vapor pressure-temperature relationship for 1,1,1-trichloroethane is presented in Table 7-17.

1,1,1-trichloroethane forms an azeotrope with methanol, containing 21.7 % by weight of methanol, which boils at 56  $^{\circ}$ C.

1,1,2-trichloroethane forms azeotropes with methanol (97 %; bp, 64.5 °C), tetrachloroethylene (57 %; bp, 112 °C) and ethanol (70 %; bp, 77.8 °C).

Both trichloroethane isomers are miscible with chlorinated solvents and are soluble in the other common organic solvents. Both isomers are solvents for a wide range of organic materials and compounds.

#### 7.8.3 CHEMICAL PROPERTIES

1,1,1-trichloroethane decomposes at temperatures in the range 360-440 °C to give 1,1-dichloroethylene and hydrogen chloride.

TABLE 7-16

# PHYSICAL PROPERTIES OF THE

### TRICHLOROETHANE ISOMERS

	1,1,1-ISOMER	1,1,2-ISOMER
Molecular Formula	CH3CC13	CH <sub>2</sub> C1-CHC1 <sub>2</sub>
Physical State	liquid	liquid
Molecular Weight	133.41	133.41
Melting Point, °C	-30.41	-36.5
Boiling Point, °C	74.1	113.77
Density, 20 °C, g/cm <sup>3</sup>	1.3390	1.4397
Refractive Index, $n_{D}^{20}$	1.4379	1.4714
Viscosity, mPa.s 15 °C 20 °C 30 °C	0.903 - 0.725	1.20
Surface Tension, mN/m 15 °C 20 °C 30 °C 113 °C	26.17 25.56 24.25	33.57
Specific Heat, J/g, °C av., -15 → + 26 °C 20 °C	1.067	- 1.130
Thermal Conductivity, W/m.°C liquid, 20 °C	-	0.135
Heat of Combustion, vapor, MJ/mol	, <del>14</del> ./	1.098
Coefficient of Cubical Expansion av., 0-25 °C	-	0.0010

# TABLE 7-16 (cont.)

Steam Distillation Point, 101.3 kPa, °C	-	85.4
Solubility in Water at 20 °C, g/100 g H <sub>2</sub> 0	0.44	0.45
Solubility of Water in Trichloroethane at 20 °C, g/100 g trichloroethane	0.05	0.05
C.A.S. Registry Number *	71-55-6	79-00-5
Synonyms	Chlorothene Methyl Chloroform Methyltrichloro- methane	Vinyl trichlorid

<sup>\*</sup> C.A.S. Registry Number of trichloroethane (isomer unspecified) is 25323-89-1

TABLE 7-17

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR 1,1,1-TRICHLOROETHANE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
0	4.93
10	8.27
201	13.33
30	20.00
40	32.00
50	45.33
60	62.66
70	87.99
80	119.99

The vapor pressure of 1,1,2-trichloroethane at 20 °C is 2.23 kPa.

$$CH_3CCl_3 \rightarrow CH_2=CCl_2 + HCl$$

This decomposition has been shown to occur via a unimolecular and radical chain mechanism simultaneously (1). At temperatures above 150 °C, the above reaction takes place in contact with cobalt, nickel, platinum, or palladium salts or oxides.

1,1,2-trichloroethane shows no appreciable decomposition, in the absence of air and water, up to 150 °C. At ambient temperatures no reaction occurs with atmospheric oxygen. When heated in the vapor phase over active charcoal impregnated with barium chloride, 1,1,2-trichloroethane decomposes to a mixture of 1,1- and 1,2-dichloroethylene, the proportion of the latter increasing with increase in temperature; at 500 °C the mixture contains 85 % 1,2-dichloroethylene.

1,1,1-trichloroethane has little effect on the common construction metals when dry, but in the presence of water or steam, corrosion occurs due to the formation of hydrogen chloride. When heated with water under pressure at 75-160 °C, in the presence of sulfuric acid or metal chlorides, 1,1,1-trichloroethane decomposes to give acetyl chloride, acetic acid or acetic anhydride, depending on the amount of water present.

1,1,2-trichloroethane, at its boiling point, is hydrolysed by water. It is dehydrochlorinated to 1,1-dichloroethylene on heating with aqueous sodium hydroxide solution, and to 1,1- and 1,2-dichloroethylene by an aqueous calcium hydroxide suspension. Dehydrochlorination may also be effected by passing 1,1,2-trichloroethane over activated charcoal at high temperature, yielding 1,1- and 1,2-dichloroethylene.

l,l,l-trichloroethane, in the absence of stabilizers, is oxidized by the atmosphere at elevated temperatures, with phosgene among the oxidation products.

By reaction with an aqueous calcium hydroxide suspension, 1,1,1trichloroethane is dehydrochlorinated to 1,1-dichloroethylene.

Both isomers, on chlorination in the vapor phase, form 1,1,1,2-tetrachloroethane. 1,1,1-trichloroethane also forms small quantities of penta- and hexachloroethane in this reaction.

The reaction of 1,1,1-trichloroethane with hydrogen fluoride at 144 °C in the absence of a catalyst results in formation of 1,1-dichloro-1-fluoroethane and 1-chloro-1,1-difluoroethane.

$$2CH_3CC1_3 + 3HF \rightarrow CH_3CFC1_2 + CH_3CF_2C1 + 3HC1$$

Hydrofluorination of 1,1,2-trichloroethane requires the presence of a catalyst, stannous chloride, at a concentration of 2.5 wt %, yielding 1,2-dichloro-l-fluoro-ethane.

#### 7.9 TETRACHLOROETHANE

#### 7.9.1 INTRODUCTION

There are two isomers of tetrachloroethane; 1,1,1,2-tetrachloroethane, CCl<sub>3</sub>CH<sub>2</sub>Cl, and 1,1,2,2-tetrachloroethane, CHCl<sub>2</sub>CHCl<sub>2</sub>. Both are dense, colorless, nonflammable liquids with heavy sweet odors. 1,1,1,2-tetrachloroethane is of no commercial interest, and few of its properties have been investigated.

1,1,2,2-tetrachloroethane was discovered in 1869 by Berthelot and Jungfleish.

#### 7.9.2 PHYSICAL PROPERTIES

The physical properties of 1,1,2,2-tetrachloroethane are listed in Table 7-18 (1, 2). Its vapor pressure-temperature relationship is presented in Table 7-19 (1).

Reported physical properties for 1,1,1,2-tetrachloroethane (2) are: melting point, -70.2 °C; boiling point, 130.5 °C; density, 1.54064 g/cm $^3$ ; refractive index,  $n_D^{20}$ , 1.4821. It is reported to be soluble in chlorinated solvents, ethanol, ether, acetone and benzene, and slightly soluble in water.

Twenty-six binary azeotropes of 1,1,2,2-tetrachloroethane are known. The azeotrope with water contains 31.1 % H $_2$ 0 and boils at 93.2 °C at 97.33 kPa.

1,1,2,2-tetrachloroethane is miscible with the chlorinated solvents and is a powerful solvent for a large number of natural organic materials and for a wide range of organic compounds. It is also a solvent for

TABLE 7-18

# PHYSICAL PROPERTIES OF 1,1,2,2-TETRACHLOROETHANE

Molecular Formula	CHC12CHC12
Physical State	Liquid
Molecular Weight	167.85
Melting Point, °C	-36
Boiling Point, °C	146.2
Density, 20 °C, g/cm <sup>3</sup>	1.5953
Refractive Index, n <sub>D</sub> <sup>20</sup>	1.4940
Viscosity, mPa.s 10 °C 15 °C 20 °C 30 °C	2.059 1.844 1.770 1.456
Surface Tension, mN/m 20 °C 40 °C	36.04 33.30
Latent Heat of Vaporization, 146.2 °C, J/g	229.7
Specific Heat, J/g, °C liquid vapor, 146.2 °C	1.121 0.920
Critical Temperature, °C	388
Thermal Conductivity W/m.°C	0.135
Heat of Formation, vapor, kJ/mol	158.9
Dielectric Constant, liquid, 20 °C	8.00
Dipole Moment, esu	1.85 x 10 <sup>-18</sup>

# TABLE 7-18 (cont.)

Coefficient of Cubical Expansion, av., 0-30 °C	0.00103
Steam Distillation Point, 101.3 kPa, °C	93.7
Solubility in Water at 25 °C, g/100 g $\rm H_2^{0}$	0.29
Solubility of Water in 1,1,2,2-tetrachloroethane at 25 °C, g/100 g 1,1,2,2-tetrachloroethane	1.13
C.A.S. Registry Number *	79-34-5
Synonyms	Sym-tetrachloroethane Acetylene tetrachloride

 $\star$  C.A.S. Registry Numbers for tetrachloroethane is 25322-30-7 and for 1,1,1,2-isomer is 630-20-6

### TABLE 7-19

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR 1,1,2,2-TETRACHLOROETHANE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
32	1.33
45	2.60
60	5.33
70	8.27
91	18.66
104	29.33
118	46.66
128	62.66
138	82.66
146.2	101.32

sulfur (100 g/100 g tetrachloroethane at 120 °C) and a number of other inorganic compounds, eg sodium sulfite.

#### 7.9.3 CHEMICAL PROPERTIES

1,1,2,2-tetrachloroethane is stable even at high temperatures, in the absence of air, moisture and light. When exposed to air, dehydrochlorination slowly takes place forming trichloroethylene and traces of phosgene. Under pyrolytic conditions, 1,1,2,2-tetrachloroethane splits off hydrogen chloride and chlorine, with trichloroethylene, tetrachloroethylene, pentachloroethane, and hexachloroethane being formed. It decomposes to yield dichloroacetyl chloride under the combined action of UV radiation and air or oxygen.

Strong acids do not affect 1,1,2,2-tetrachloroethane at ambient and slightly elevated temperature. Fuming sulfuric acid reacts to form glyoxal sulfate.

1,1,2,2-tetrachloroethane is dehydrochlorinated to trichloroethylene by weak alkaline solutions. However, on heating with strong alkali, in solution or solid form, dichloroacetylene is formed and explosion may occur.

1,1,2,2-tetrachloroethane is reduced, in the presence of boiling water or steam, to 1,2-dichloroethylene, by contact with metals such as iron, aluminium, or zinc in the form of powder or filings.

Chlorination of 1,1,2,2-tetrachloroethane to hexachloroethane takes place only slowly at 100 °C. Chlorination catalysts, such as activated charcoal, ferric chloride, aluminium chloride or stannous chloride, do

not affect the rate of this reaction. At 25 °C, no reaction occurs at all.

Chlorination is greatly accelerated by irradiation with light of wavelength 315-354 nm, the rate being proportional to the square root of light intensity (1).

The action of chlorine on 1,1,2,2-tetrachloroethane over activated charcoal at temperatures above 400 °C, yields carbon tetrachloride.

$$CHC1_2$$
 -  $CHC1_2$  +  $3C1_2$   $\rightarrow$   $2CC1_4$  +  $2HC1$ 

A variation of this reaction yields tetrachloroethylene (1).

### 7.10 DICHLOROETHYLENE

#### 7.10.1 INTRODUCTION

There are three isomers of dichloroethylene; 1,1,-dichloroethylene (vinylidene chloride),  $CH_2=CCI_2$ , and cis- and trans-1,2-dichloroethylene, CHCl=CHCl. All isomers are clear, colorless, volatile liquids with sweetish odors.



I,l-dichloroethylene

cis-1,2-dichloroethylene

trans-1,2-dichloroethylene

1,2-dichloroethylene is only of minor technological importance.

### 7.10.2 PHYSICAL PROPERTIES

The physical properties of the dichloroethylene isomers are listed in Table 7-20 (1, 2). The vapor pressure-temperature relationships for the three isomers are presented in Table 7-21.

1,1-dichloroethylene is miscible with most organic solvents.

Trans-1,2-dichloroethylene forms a ternary azeotrope, containing 1.4% ethanol and 1.10% water, boiling at 44.4%C; the corresponding ternary azeotrope of the cis- isomer contains 6.65% ethanol and 2.85% water, boiling at 53.8%C.

TABLE 7-20

PHYSICAL PROPERTIES OF THE DICHLOROETHYLENE ISOMERS

	1,1-ISOMER	CIS-1,2-ISOMER	TRANS-1,2-ISOMER
Molecular Formula	CH <sub>2</sub> =CCl <sub>2</sub>	CHC1=CHC1	CHC 1=CHC 1
Physical State	liquid	liquid	liquid
Molecular Weight	96.94	96.94	96.94
Melting Point, °C	-122.1	-81.47	-49.44
Boiling Point, °C	31.8	60.2	47.7
Density, 20 °C, g/cm <sup>3</sup>	1.213	1.2837	1.2565
Refractive Index, n <sup>20</sup> D	1.4249	1.4490	1.4454
Viscosity, mPa.s -50 °C -25 °C 0 °C 10 °C 20 °C	0.33	1.156 0.791 0.577 0.516 0.467	1.005 0.682 0.498 0.447 0.404
Surface Tension, 20 °C, mN/m	-	25	28
Latent Heat of Vaporization bp, J/g	on, 280.3	311.7	297.9
Specific Heat, 20 °C, J/g, °C	1.130	1.176	1.159
Critical Temperature, °C	-	271.0	243.3
Critical Pressure, MPa	L	-	5.51
Thermal Conductivity, W/m.°C	-	0.1467	0.1266

# TABLE 7-20 (cont.)

	1,1-ISOMER	CIS-1,2-ISOMER	TRANS-1,2-ISOMER
Dielectric Constant, 16 °C 20 °C	4.67	9.31	- 2.15
Dipole Moment, esu	+	$1.85 \times 10^{-18}$	-
Coefficient of Cubical Expansion, av., 15-45 °C		0.00127	0.00136
Flash Point, °C	-23	~	-
Autoignition Temperature, °C	570	-	-
Explosive Limits in air, vol %	5.6 - 13	-	-
Heat of Polymerization, kJ/mol	60.67	-	-
Solubility in Water, 25 °C, g/100 H <sub>2</sub> 0 20 °C, g/100 cm <sup>3</sup> H <sub>2</sub> 0	0.04	0.35	0.63
Solubility of Water in Isomer,		i.	
25 °C, g/100 g 20 °C, g/100 cm <sup>3</sup>	0.4	0.55	0.55
Steam Distillation Point 101.3 kPa, °C	-	53.8	45.3
Boiling Point of Binary Azeotropes, °C with water			
1.9 % H <sub>2</sub> 0 3.35 % H <sub>2</sub> 0 with methanol	-	55.3	45.3
13 % CH <sub>3</sub> OH with ethanol	-	51.5	-
6.0 % C <sub>2</sub> H <sub>5</sub> OH 9.8 % C <sub>2</sub> H <sub>5</sub> OH	2	- 57.7	46.5

# TABLE 7-20 (cont.)

C.A.S. Registry Number \*

75-35-4

540-59-0

156-59-2

Synonyms

Vinylidene chloride l,l-dichloro-

Acetylene dichloride 1,2-dichloro-

ethane ethane

\* C.A.S. Registry Number for dichloroethylene (isomer unspecified) is 25323-30-2

TABLE 7-21

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE DICHLOROETHYLENE ISOMERS

TEMPERATURE, °C	×	VAPOR PRESSURE, kPa	
	1,1-ISOMER	CIS-1,2-ISOMER	TRANS-1,2-ISOMER
-20	10.66	2.67	5.33
-10	18.00	5.07	8.53
0	28.66	8.67	15.07
10	> <b>-</b>	14.67	24.66
20	66.00	24.00	35.33
30	95.99	33.33	54.66
31.8	101.32	=	-
40	-	46.66	76.66
47.7	-	66.66	101.32
60.2	-	101.32	_

The proportions of trans- and cis-1,2-dichloroethylene isomers in a mixture depends upon the conditions of manufacture. A typical product boils in the range 45-60 °C, has a flash point of about 6 °C, and explosive limits in air of 0.7-12.8 vol % (1). The isomers and their mixtures are powerful solvents for many substances, eg rubber.

#### 7.10.3 CHEMICAL PROPERTIES

#### 7.10.3.1 REACTIONS OF THE 1,1-ISOMER

I,1-dichloroethylene undergoes autooxidation, even in the dark, in the presence of air or oxygen to form a perioxide. I,1-dichloroethylene processes the polymerizable group  $\mathrm{CH}_2^-$  and thus, forms long-chain polymers in the presence of the peroxide formed by its own oxidation.

Chlorination of 1,1-dichloroethylene at 40-50 °C gives 1,1,1,2-tetrachloroethane.

l,l-dichloroethylene reacts with hydrogen chloride, in the presence of anhydrous aluminium chloride, to yield l,l,l-trichloroethane.

#### 7.10.3.2 REACTIONS OF THE 1,2-ISOMER

Trans-1,2-dichloroethylene is more chemically reactive than the cisisomer. In the presence of bromine or alumina at high temperatures, one isomer can be partially converted to the other.

Weak alkalis do not affect 1,2-dichloroethylene, but on boiling with aqueous sodium hydroxide solution, explosion may occur due to formation of monochloroacetylene.

1,2-dichloroethylene is slowly hydrolyzed by water in the absence of stabilizers, forming hydrochloric acid. This reaction causes metal corrosion if in contact with the solvent under these conditions.

1,2-dichloroethylene is oxidized by oxygen, in the presence of concentrated sulfuric acid, forming chloroacetyl chloride.

Under high pressures, in the presence of organic peroxides, 1,2-dichloroethylene dimerizes to tetrachlorobutene. Formation of long-chain polymers occurs at pressures of the order of 810 MPa.

#### 7.11 TRICHLOROETHYLENE

#### 7.11.1 INTRODUCTION

Trichloroethylene,  $CHCl=CCl_2$ , is a colorless, volatile liquid with a sweet odor. It is nonflammable under conditions of normal use.

Trichloroethylene was first prepared by Fischer in 1864, in the course of experiments in the reduction of hexachloroethane with hydrogen.

Because of its properties of nonflammability, volatility and powerful solvent action for fats, greases, and waxes, trichloroethylene has found its main applications as a vapor-degreasing and dry-cleaning solvent. It is a powerful solvent for a large number of other natural and synthetic organic substances.

#### 7.11.2 PHYSICAL PROPERTIES

The physical properties of trichloroethylene are listed in Table 7-22 (1, 2). Vapor pressure and viscosity relationships with temperature for trichloroethylene are presented in Tables 7-23 and 7-24 respectively (1).

Trichloroethylene is completely miscible with all of the common organic solvents. It is itself a solvent for benzyl cellulose, bitumens, caffeine, chlorinated rubber, ethyl cellulose, naphthalene, naphthols, oleic acid, paraffin wax, polystyrene, polyvinyl acetate, unvulcanized natural rubber, stearic acid, sulfur, thymol, vegetable oils, petrolatum, and a number of other substances used commonly in industry.

Trichloroethylene forms a series of binary azeotropes; these are listed in Table 7-25.

# TABLE 7-22

# PHYSICAL PROPERTIES OF TRICHLOROETHYLENE

Molecular Formula	CHC1=CHC1 <sub>2</sub>
Physical State	liquid
Molecular Weight	131.39
Melting Point, °C	-73
Freezing Point, °C	-86.4
Boiling Point, °C	86.7
Density, 20 °C, g/cm <sup>3</sup>	1.4642
Refractive Index, n <sub>D</sub> <sup>20</sup>	1.4773
Surface Tension, 30 °C, mN/m	29
Vapor Density, bp, 101.3 kPa, g/1	4.45
Specific Gravity, vapor, bp, 101.3 kPa (air = 1)	4.54
Specific Heat, 80 °C, 101.3 kPa, J/g. °C liquid vapor	0.941 0.653
Critical Temperature, °C	271
Critical Pressure, MPa	5.02
Thermal Conductivity, W/m.°C liquid vapor, bp	0.139 0.00834
Coefficient of Cubical Expansion, liquid, av., 0-40 °C	0.00117
Dielectric Constant, liquid, 16 °C	3.42
Dipole Moment, esu	$0.9 \times 10^{-18}$

# TABLE 7-22 (cont.)

Heat of Formation, kJ/mol liquid vapor	4.18 -29.29
Latent Heat of Evaporation, bp, J/g	239.3
Viscosity, vapor, 60 °C, mPa.s	0.0103
Solubility in Water, g/100 g H <sub>2</sub> 0 25 °C 60 °C	0.11 0.125
Solubility of Water in trichloroethylene, g/100 g trichloroethylene 0 °C 25 °C 60 °C	0.01 0.033 0.080
C.A.S. Registry Number	79-01-6
Synonyms	Ethylene trichloride Tri Trilene

# TABLE 7-23

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR TRICHLOROETHYLENE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
-20	0.72
-10.8	1.44
0	2.68
10	4.69
20	7.71
30	12.53
40	19.57
50	28.26
60	40.76
86.7	101.32

TABLE 7-24

# VISCOSITY-TEMPERATURE RELATIONSHIP FOR LIQUID TRICHLOROETHYLENE

TEMPERATURE, °C	VISCOSITY, mPa.s
-80	2.95
-70	2.10
-60	1.68
-30	1.02
-20	0.9
0	0.7
20	0.58
40	0.48
60	0.42

TABLE 7-25

# AZEOTROPES OF TRICHLOROETHYLENE

SECOND COMPONENT	BP OF AZEOTROPE, °C	TRICHLOROETHYLENE WEIGHT %
2-chloroethanol	86.55	97.5
		97.0
n-butanol	86.65	
glacial acetic acid	86.50	96.2
water	73.00	93.0
tert-amyl alcohol	86.67	92.5
iso-butanol	85.40	91.0
methyl carbonate	85.95	90.0
2-iodopropane	<86.50	<88.0
sec-butanol	84.20	85.0
allyl alcohol	. 80.90	84.4
n-propanol	81.75	83.0
ethanol	70.90	72.5
acetonitrile	74.60	71.0
iso-propanol	75.50	70.0
tert-butanol	75.80	∿67.0
ethyl nitrate	83.50	62.0
diethoxymethane	89.20	53.5
1,2-dichloroethane	82.10	43.5
n-propyl formate	79.50	20.0

#### 7.11.3 CHEMICAL PROPERTIES

#### 7.11.3.1 DEGRADATION REACTIONS

Pure trichloroethylene, containing a suitable stabilizer, is stable in the presence of air, moisture, light, and in contact with the common construction metals up to 130 °C. Heated to 700 °C and above, the vapor decomposes giving a mixture of dichloroethylene, perchloroethylene, carbon tetrachloride, chloroform and methyl chloride.

When heated strongly with air, trichloroethylene vapor is completely oxidized to carbon dioxide and hydrogen chloride. With ozone, an explosive ozonide is formed, which decomposes to hydrogen chloride, phosgene, carbon monoxide, and chlorine peroxide.

The oxidative breakdown of trichloroethylene by atmospheric oxygen is its most important reaction for industrial usage considerations. This decomposition is enhanced by elevated temperatures or exposure to light, especially UV radiation. The oxidation follows two main courses, the initial stages of which are the formation of oxygen compounds.

$$\begin{array}{c|c}
C & 1 & 2 & 0 & 0 \\
C & 1 & 1 & 0 & 0 \\
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(1) & C & 1 & 1 & 0 \\
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(1) & C & 1 & 1 & 0 \\
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A small amount of hexachlorobutylene is also formed by dimerization of the trichloroethylene. Over 80 % of the initial oxidation products are compound (I). These compounds (I) and (II) are sufficiently stable to be isolated by distilling off the trichloroethylene at reduced pressure. Both compounds are highly explosive, compound (I) yielding dichloroacetyl chloride, Cl<sub>2</sub>HCOCl and compound (II) yielding phosgene, carbon monoxide and hydrogen chloride. Their sudden decomposition is promoted by the introduction of impurities, and particularly by the presence of oxidation stabilizers when these are present in too low a concentration to inhibit formation of compounds (I) and (II).

The degree of oxidative breakdown of trichloroethylene is dependent on temperature, area of liquid surface exposed, oxygen concentration at the vapor-liquid interface, and the concentration of oxidation catalysts which may be present. In the presence of water, the dichloroacetyl chloride formed is decomposed to dichloroacetic and hydrochloric acids, increasing the corrosive action of the trichloroethylene solvent on metals with which it may be in contact.

Mixtures of compounds are usually used as synergistic stabilizers in trichloroethylene. A typical mixture contains diisopropylamine, and alkyl-p-hydroxyanisole, phenol, thymol, o-cresol, n-butane, tetra-hydrofuran, and N-methylpyrrole.

#### 7.11.3.2 REACTIONS WITH ACIDS AND BASES

Water does not hydrolyse trichloroethylene under normal conditions of use.

Trichloroethylene reacts with alkaline hydroxides at 150 °C, under pressure, to give glycolic acid, CH<sub>2</sub>OHCOOH. Strong alkalis, eg sodium hydroxide, dehydrochlorinate trichloroethylene on heating, producing explosive and flammable chloroacetylenes.

Sodium carbonate does not react with trichloroethylene, and is thus sometimes used to remove acid and moisture during solvent recovery. Aqueous ammonia also does not react under normal conditions.

Trichloroethylene reacts with 90 % sulfuric acid producing mono-chloroacetic acid, CH<sub>2</sub>ClCOOH. Cold hydrochloric and nitric acids do not react with trichloroethylene, but strong, hot nitric acid reacts violently, producing complete oxidative decomposition.

#### 7.11.3.3 HALOGENATION REACTIONS

Trichloroethylene is readily chlorinated in the presence of catalysts at temperatures below its boiling point, yielding pentachloro- and hexachloroethane. A mixture of these two compounds is also obtained by photochlorination of trichloroethylene under UV light.

Bromination of trichloroethylene yields 1,2-dibromo-1,1,2-trichloroethane.

Hydrogen fluoride, in the presence of antimony trifluoride as catalyst, fluorinates trichloroethylene to 2-chloro-1,1,1-trifluoroethane. At ordinary temperatures, trichloroethylene reacts with elemental fluorine producing a mixture of chlorofluoroderivatives of ethane, ethylene and butane.

#### 7.11.3.4 REACTIONS WITH ALUMINIUM AND ALUMINIUM CHLORIDE

Aluminium, especially in a divided state, can initiate violent reactions in unstabilized trichloroethylene. Charring, slight explosions, and even formation of incandescent masses can occur, with copious evolution of hydrogen chloride fumes. This reaction is believed to be caused by initial formation of aluminium chloride, which then acts as a Freidel-Crafts catalyst for self condensation of the trichloroethylene to pentachlorobutadiene.

Trichloroethylene can form hexachlorobutene, CCl<sub>2</sub>=CHCHClCCl<sub>3</sub> under controlled conditions in the presence of aluminium chloride catalyst.

It can also be reacted with carbon tetrachloride over aluminium chloride, yielding heptachloropropane.

$$CC1_4 + CHC1 = CC1_2 \rightarrow CC1_3 CHC1CC1_3$$

Aluminium chloride also catalyses the reaction, at 50 °C, of trichloroethylene with hydrogen chloride. The reaction products are a mixture of pentachlorobutadiene, 1,1,1,2- and 1,1,2,2-tetrachloroethane, and some hexachlorobenzene.

#### 7.11.3.5 POLYMERIZATION REACTIONS

It has been reported (1) that trichloroethylene will copolymerize with vinyl chloride under pressure at 40-60 °C in the presence of ammonium persulfate and sodium bisulfite catalyst. The polymer obtained

is claimed to be suitable as a coating material. The copolymerization of trichloroethylene with 1,3-butadiene and homologs has been patented (1).

Dimers and trimers of trichloroethylene, formed by heating at  $150\text{--}200~^{\circ}\text{C}$  under pressure in the presence of peroxide catalysts, have been reported (1).

#### 7.12 PERCHLOROETHYLENE

#### 7.12.1 INTRODUCTION

Perchloroethylene (tetrachloroethylene),  $CCl_2 = CCl_2$ , is a colorless, clear, heavy liquid with a pleasant ethereal odor. It is a powerful solvent for a large number of organic substances.

The principal application of perchloroethylene is as a dry-cleaning solvent; it is also used for metal degreasing, as a solvent for a number of organic materials such as fats, oils, tars, rubber and gums, and in the synthesis of trichloroacetic acid.

Perchloroethylene was first prepared by Faraday in 1821, by the thermal decomposition of hexachloroethane. In 1840, Regnault prepared the compound by passing carbon tetrachloride vapor through a red-hot tube, and also by reduction of hexachloroethane with alcoholic potassium hydrosulfide. Combes produced perchloroethylene in 1887 by prolonged heating of chloral with anhydrous aluminium chloride. In 1894, Meyer isolated it as a by-product in the industrial production of carbon tetrachloride from carbon disulfide (1).

#### 7.12.2 PHYSICAL PROPERTIES

The physical properties of perchloroethylene are listed in Table 7-26 (1, 2). The vapor pressure-temperature relationship for perchloroethylene is presented in Table 7-27.

Perchloroethylene forms about sixty binary azeotropic mixtures; some of these are presented in Table 7-28. Only one ternary azeotrope is known consisting of 45 % isoamyl formate, 25 % paraldehyde and 30 % perchloroethylene, which boils at 117.6 °C.

# TABLE 7-26

# PHYSICAL PROPERTIES OF PERCHLOROETHYLENE

Molecular Formula	cc1 <sub>2</sub> =cc1 <sub>2</sub>
Physical State	liquid
Molecular Weight	165.83
Melting Point, °C	-19.0
Freezing Point, °C	-22.7
Boiling Point, °C	121.2
Density, g/cm <sup>3</sup> 10 °C 15 °C 20 °C 30 °C 120 °C	1.63120 1.63109 1.62270 1.60640 1.44865
Refractive Index, n <sub>D</sub> <sup>20</sup>	1.5053
Vapor Density, bp, 101.3 kPa, g/l	5.8
Viscosity, vapor, 60 °C, mPa.s	0.0099
Viscosity, liquid, mPa.s 15 °C 20 °C 25 °C 30 °C 50 °C 75 °C	0.932 0.880 0.839 0.798 0.657 0.534
Surface Tension, mN/m 15 °C 20 °C 30 °C	32.86 32.32 31.27
Specific Heat, J/g °C liquid, 20 °C vapor, 100 °C, 101.3 kPa	0.858 0.611

# TABLE 7-26 (cont.)

Thermal Conductivity, W/m.°C liquid vapor, bp	0.1266 0.00874
Heat of Combustion, kJ/mol Constant pressure, with formation of aq HCl	679.9
Constant Volume, 18.7 °C	831.8
Latent Heat of Vaporization, 121.2 °C, J/g	209.2
Critical Temperature, °C	347.1
Latent Heat of Fusion, kJ/mol	10.56
Heat of Formation, kJ/mol vapor liquid	-25.10 12.55
Dielectric Constant 15 °C 90 °C	2.353 2.134
Coefficient of Cubical Expansion, av 0-25 °C 15-90 °C	0.00102 0.001079
Solubility in Water, g/100 g H <sub>2</sub> 0	0.015
Solubility of water in perchloroethylene, g/100 g perchloroethylene	0.008
C.A.S. Registry Number	127-18-4
Synonums	Tetrachloroethylene Ethylene tetrachloride Perclene

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP FOR PERCHLOROETHYLENE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
-20.6	0.133
2.4	0.667
13.8	1.33
26.3	2.67
40.0	5.47
50.0	8.93
70.0	13.87
80.0	20.71
90.0	42.56
100.0	58.46
110.0	78.87
121.2	101.32

TABLE 7-28

# AZEOTROPES OF PERCHLOROETHYLENE

SECOND COMPONENT	BP OF AZEOTROPE, °C	PERCHLOROETHYLENE, WT. %
butyric acid	121.0	98.8
acetamide	120.5	97.4
glycol	119.1	94.0
octane	<120.5	<92.0
propionic acid	119.1	91.5
amyl alcohol	117.0	74.0
water	87.7	84.2
n-butyl acetate	120.1	79.0
ethyl carbonate	118.6	74.0
paraldehyde	118.8	68.0
acetic acid	107.4	61.5
1,1,2-trichloroethane	112.0	57.0
n-propanol	94.1	52.0
pyridine	112.9	51.5
epichlorohydrin	110.1	48.5
ethanol	76.8	<sup>~</sup> 37.0
iso-propanol	81.7	30.0

Perchloroethylene dissolves sulfur, iodine, mercuric chloride, and appreciable amounts of aluminium chloride. It is a solvent for benzoic, cinnamic, phenylacetic, phenylpropionic and salicylic acids, and a large number of organic substances such as fats, oils, tars, rubber and resins. It is miscible with the other chlorinated organic solvents and with many of the other common solvents. Perchloroethylene does not dissolve sugars, glycerol, proteins, or casein.

#### 7.12.3 CHEMICAL PROPERTIES

#### 7.12.3.1 DEGRADATION REACTIONS

Pure, stabilized perchloroethylene can be used in the presence of air, water and light, in contact with common construction metals up to about 140 °C. The unstabilized compound, in the presence of water for prolonged periods, is slowly decomposed to trichloroacetic and hydrochloric acids.

Perchloroethylene is stable up to about 500 °C in the absence of catalysts, air or moisture. At 700 °C in contact with activated carbon, it decomposes to hexachloroethane and hexachlorobenzene.

Excess hydrogen, at 22 °C in the presence of reduced nickel catalyst, totally decomposes perchloroethylene to hydrogen chloride and carbon.

### 7.12.3.2 OXIDATION REACTIONS

Perchloroethylene is unaffected by oxygen in the absence of light.

With ozone, it is decomposed to phosgene and trichloroacetyl chloride.

The latter compound is also formed on oxidation of perchloroethylene with a mixture of sulfuric and nitric acids.

In the presence of bromine or concentrated nitric acid, perchloroethylene is oxidized by oxygen to trichloroacetyl chloride. Trichloroacetyl chloride is also formed as an oxidation product of perchloroethylene by reaction with sulfur trioxide at 150 °C, and by autooxidation with air or oxygen by irradiation with UV light. The intermediate stage in the autooxidation reaction is the formation of peroxides (as for trichloroethylene).

Compound (I) rearranges to trichloroacetyl chloride and oxygen.

Compound (II) breaks down to yield two molecules of phosgene.

The reaction giving trichloroacetyl chloride takes place to a much greater extent than that producing phosgene. The autooxidation reaction is responsible for the slow decomposition of perchloroethylene in the presence of light and air. The reaction is inhibited by the same substances used to stabilize trichloroethylene.

#### 7.12.3.3 HALOGENATION REACTIONS

Photochlorination of perchloroethylene yields hexachloroethane.

Perchloroethylene is brominated to bromotrichloroethane and dibromodichloroethane by heating with aluminium bromide at 100 °C. Elemental bromine reacts to give an equilibrium mixture of tetrabromodand tetrachloroethylene.

A mixture of hydrogen and chlorine reacts with perchloroethylene at 225-400 °C in the presence of zirconium fluoride catalyst to yield 1,2,2-trichloro-1,1,2-trifluoroethane.

#### 7.12.3.4 OTHER REACTIONS

Perchloroethylene is completely decomposed by ammonia under high pressure, the products being ammonium chloride and elemental carbon.

Perchloroethylene reacts explosively with lithium butyl in petroleum ether solution, and also with metallic potassium at its melting point.

On heating perchloroethylene with o-benzenedithiol at 110-120 °C in the presence of sodium ethoxide, the compound 2,2'-bis-1,3-benzthiolene is formed.

In the presence of dibenzoyl peroxide, perchloroethylene is reported to form copolymers with styrene, vinyl acetate, methyl acrylate and acrylonitrile (1).

#### 7.13 CHLOROPRENE

#### 7.13.1 INTRODUCTION

Chloroprene (2-chloro-1,3-butadiene),  $CH_2=C(C1)CH=CH_2$ , is a colorless, mobile, volatile liquid of characteristic odor and great reactivity. It is flammable and toxic and forms explosive mixtures with air.

Chloroprene was first isolated by Carothers and Collins in 1930, who named the compound in analogy to isoprene (2-methyl-1,3-butadiene), the percursor of natural rubber. It has gained commercial importance as the raw material for the manufacture of synthetic elastomers marketed under the generic name, neoprene. Chloroprene is manufactured from monovinylacetylene, which, in turn, is manufactured from acetylene.

Other routes of manufacture using butanes, butenes or butadienes as raw materials, are known.

#### 7.13.2 PHYSICAL PROPERTIES

The physical properties of chloroprene are listed in Table 7-29 (1). Chloroprene is only slightly soluble in water but miscible with most organic solvents.

The vapor pressure-temperature relationship for chloroprene is presented in Table 7-30.

#### 7.13.3 CHEMICAL PROPERTIES

The great reactivity of chloroprene is due to the activation of the double bonds by the chlorine atom. Thus chloroprene polymerizes spontaneously at room temperature and forms cyclic dimers on prolonged standing in the presence of polymerization inhibitors. Various inorganic

## PHYSICAL PROPERTIES OF CHLOROPRENE

Molecular Formula	CH <sub>2</sub> =C(C1)CH=CH <sub>2</sub>
Physical State (STP)	liquid
Molecular Weight	88.54
Melting Point, °C	-130 <u>+</u> 2
Boiling Points, °C	
13.33 kPa 40.00 kPa 53.33 kPa 66.66 kPa 99.33 kPa 101.32 kPa (Atmos. Pressure) 182.65 kPa	6.4 32.8 40.5 46.9 58.7 59.4
Density, g/cm <sup>3</sup> 20 °C	0.9585
Refractive Index, n, 20 °C C line D line F line	1.4540 1.4583 1.4690
Critical Temperature, °C	261.7
Flash Point (ASTM, open cup), °C	-20
Latent Heat of Vaporization, J/g 0 °C 60 °C	332.6 302.5
Specific Heat, J/g.°C liquid, 0 °C liquid, 20 °C gas, 0 °C gas, 100 °C	1.243 1.314 0.782 1.038
Thermal Conductivity (t=temp.), gas, W/m.°C	$1.008 \times 10^{-4} + 0.0669 \times 10^{-5} t$
Average Coefficient of Volumetric Expansion, 20-61 °C	0.001235

# TABLE 7-29 (cont.)

Viscosity, 25 °C, mPa.s	0.394
Dipole Moment (in benzene), esu	$1.42 \times 10^{-18}$
Dielectric Constant, 27 °C	4.9
Ionization Potential, V	8.79
<pre>Intramolecular Distances (planar), nm RC = C RC = C RC-CL</pre>	0.136 0.146 <u>+</u> 0.004 0.170 <u>+</u> 0.002
Intramolecular angles (planar), °(trigonometric) $c_1c_2c_1$ $c_1c_2c_3$ $c_2c_3c_4$	122 122 127 <u>+</u> 3
C.A.S. Registry Number	126-99-8
Synonyms	2-chloro-1,3-butadiene 2-chlorobutadiene

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP

## FOR CHLOROPRENE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
0	9.8
10	15.5
20	23.9
30	35.6
40	51.9
50	73.7
60	102.7
70	140.2
80	188.1
90	248.2
100	322.9

Calculate by 
$$log_{10} p = \frac{1545.3}{T} + 7.527$$

where p = vapor pressure in mm Hg<sup>2</sup>

T = temperature in K

1 mm Hg = 133.322 Pa



and organic compounds add readily to the double bonds. Usually 1,4-addition is favoured, but exceptions to this are known. Additions occur by homopolar (free-radical) and heteropolar (ionic) mechanisms.

The chlorine atom in chloroprene is tightly bound and thus very unreactive. Chloroprene does not react with Grignard reagents, and on refluxing with concentrated alcoholic sodium hydroxide or alcoholic silver nitrate, only traces of chlorine are split off.

#### 7.13.3.1 ADDITION REACTIONS

# 7.13.3.1.1 REACTIONS WITH OXYGEN, SULFUR, SULFUR DIOXIDE, AND NITROGEN DIOXIDE

Chloroprene combines readily with oxygen even at low temperatures to form a polymeric peroxide of the form:

$$[-cH_2c(c1)=cHcH_2OOCH_2c(c1)=cHcH_2OO-]_n$$

This autooxidation reaction is subject to catalysis by light, peroxides and hydrogen chloride, and inhibition by antioxidants such as phenyl-2-naphthylamine, pyrogallol, phenothiazine or hydroquinone. In the absence of light practically no autooxidation occurs. Above 0 °C, the chloroprene peroxide may decompose and catalyse the "spontaneous" polymerization of chloroprene. On rigorous exclusion of all traces of oxygen, no "spontaneous" polymerization occurs.

Chloroprene reacts with sulfur in the vapor phase to give 3-chlorothiophene.

On reaction with  $N_2^{0}_4$ , two isomeric addition compounds are formed, 2-chloro-1,4-dinitro-1-butene and 3-chloro-1,2-dinitro-3-butene, which have been used as polymerization inhibitors, especially against "popcorn" polymerization (see below).

### 7.13.3.1.2 HALOGENATION REACTIONS

The chlorination of chloroprene in chloroform solution at about

-10 °C gives an 80 % yield of the 1,4-addition product, 1,2,4-trichloro
2-butene, and a small amount of the 3,4-addition product, 2,3,4-trichloro
1-butene. Bromine yields exclusively under these conditions the

1,4-addition product, 1,4-dibromo-2-chloro-2-butene.

The addition of concentrated hydrochloric acid to chloroprene, in the presence of cuprous and ammonium chloride, gives 1,3-dichloro-2-butene by 1,4-addition, and similarly hydrogen bromide in glacial acetic acid adds to chloroprene at -5 °C to give 1-bromo-3-chloro-2-butene.

Hypochlorous acid and its esters add to chloroprene predominantly in the 1,4-manner. When hypobromites or hypoiodites are added to chloroprene, 3,4-addition predominates. This is believed to be due to the large steric effects associated with the bromine and iodine atoms.

#### 7.13.3.1.3 DIELS-ALDER ADDITIONS

In contrast to its great tendency to polymerize, the reactivity of chloroprene in the Diels-Alder reaction is considerably less than that of isoprene and butadiene. The reaction with maleic anhydride and with 1,4-naphthoquinone are used to identify chloroprene.

Oxidation of 4-chloro-4-cyclohexene-1,2-dicarboxylic acid with hot 70 % nitric acid gives butane-1,2,3,4-tetracarboxylic acid.

Many other Diels-Alder reactions of chloroprene have been described. In all of these reactions a small amount of polymerization inhibitor is usually added, eg hydroquinone.

#### 7.13.3.2 FREE RADICAL REACTIONS

Free radical attacks on chloroprene start at the terminal carbon atom, preferentially the 1-carbon atom. Free radical reactions of chloroprene are generally much faster than for other monomeric compounds.

The addition of mercaptans, such as ethanethiol and benzenethiol, gives the 1,4 and 4,1-adducts,  $RSCH_2C(C1)=CHCH_3$  and  $RSCH_2CH=C(C1)CH_3$  in ratios from 75:25 to 95:5, the former ratios predominating with aliphatic and the latter with aromatic mercaptans. The deciding factor is the stability of the intermediate allylic free radicals.

#### 7.13.3.3 MISCELLANEOUS REACTIONS

In the presence of Freidel-Crafts catalysts such as ferric chloride, aluminium chloride, stannous chloride or zinc chloride, chloroprene gives adducts mainly by 1,4-addition with compounds such as 1,3-dichloro-2-butene, 2-chloro-3-pentene and  $\alpha$ -chloromethyl ether.

The reactions proceed by a stepwise cationic mechanism, and with excess of the additive, mainly low molecular weight polymers are formed.

With dichlorophenyl phosphine, chloroprene yields a five-membered ring adduct which hydrolyses to a cyclic phosphine oxide that has insecticide activity.

#### 7.13.3.4 POLYMERIZATION REACTIONS

Chloroprene polymerizes spontaneously even at room temperature by a free radical mechanism at a rate about 700 times faster than isoprene. A plastic, soluble polymer is formed first (" $\alpha$ -polychloroprene) which continues to polymerize to an insoluble polymer (" $\mu$ -polychloroprene).

The polymerization proceeds by heat-to-tail addition and is subject to catalysis by light, peroxides and other free radical initiators, and to retardation by inhibitors such as quinones, mercaptans, and aromatic nitrocompounds.

$$R^{\circ} + CH_{2} = C(C1) CH = CH_{2} \rightarrow RCH_{2}C(C1) = CHCH_{2}$$

$$C_{4}H_{5}C1$$

$$RCH_{2}C(C1) = CHCH_{2}CH_{2}C(C1) = CHCH_{2}$$

$$C_{4}H_{5}C1$$

RCH<sub>2</sub>C(Cl)=CHCH<sub>2</sub>CH<sub>2</sub>C(Cl)=CHCH<sub>2</sub>CH<sub>2</sub>C(Cl)=CHCH<sub>2</sub> → high polymers

The properties of the high molecular weight elastomers, marketed as neoprenes, can be regulated by adjusting the polymerization temperature, polymerization medium, conversion level, and the amount and type of chain-transfer agents and comonomers.

Under certain conditions, especially under UV illumination and in the presence of certain metals such as sodium, chloroprene polymerizes autocatalytically in the vapor and liquid phases to a hard, insoluble "popcorn-like" mass, called "w-polychloroprene". The latter has a three dimensional structure and presents serious hazards to equipment and safety, and, in addition, if present in the final rubber, affects polymer quality. Certain nitric oxide-type compounds act as inhibitors for "popcorn" polymer formation. Chloroprene can also be polymerized by non-free radical mechanisms.

#### 7.14 CHLOROBENZENE

#### 7.14.1 INTRODUCTION

Chlorobenzene,  ${}^{C}_{6}{}^{H}_{5}{}^{C}_{1}$ , is a colorless, mobile liquid with a characteristic odor of almonds. It is the first derivative of the chlorination of benzene.

The chlorination of benzene is believed to have been first studied by Jungfleisch in 1868. However, in 1851 Laurent and Gerhardt produced chlorobenzene by reacting phenol with phosphorus pentachloride.

#### 7.14.2 PHYSICAL PROPERTIES

The physical properties of chlorobenzene are listed in Table 7-31 (1, 2), and its vapor pressure-temperature relationship is presented in Table 7-32. Azeotropic mixtures of chlorobenzene are given in Table 7-33.

Chlorobenzene is completely miscible with many organic liquids, such as alcohols, ethers, aliphatic and aromatic hydrocarbons, and the chlorinated solvents. It dissolves many natural organic materials such as oils, fats, resins and rubber.

#### 7.14.3 CHEMICAL PROPERTIES

Chlorobenzene is unaffected by air, moisture or light under ambient conditions, and does not split off chlorine even after prolonged boiling.

If chlorobenzene vapor is passed through a red-hot tube, 4,4'-dichlorobiphenyl is formed, as well as 4-chlorobiphenyl, 1,4-diphenyl-benzene, and biphenyl.

# PHYSICAL PROPERTIES OF CHLOROBENZENE

Molecular Formula	C6H5C1
Physical State	liquid
Molecular Weight	112.56
Melting Point, °C	-45.6
Boiling Point, °C	131.5
Steam Distillation Point, °C	90
Density, 20 °C, g/cm <sup>3</sup>	1.1058
Refractive Index, $n_{D}^{20}$	1.5241
Surface Tension, mN/m 15 °C 20 °C	33.86 33.28
Critical Temperature, °C	359.2
Critical Pressure, MPa	4.53
Critical Density, g/cm <sup>3</sup>	0.3654
Explosive Limits in Air, vol % lower, 100 °C upper, 150 °C	1.8
Flash Point, °C	24
Dielectric Constant 20 °C 70 °C 106 °C at bp	5.6493 4.886 4.435 4.144
Dipole Moment (dil. benzene soln), esu	$1.58 \times 10^{-18}$
Heat of Combustion (at const. pressure), kJ/mol	3196.07

# TABLE 7-31 (cont.)

Latent Heat of Vaporization, kJ/mol	36.53
Viscosity, mPa.s 15 °C 30 °C 60 °C 120 °C 130 °C	0.844 0.711 0.512 0.313 0.292
C.A.S. Registry Number	108-90-7
Synonyms	Monochlorobenzene

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP

# FOR CHLOROBENZENE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
0	0.40
20	1.20
40	3.47
60	8.67
80	19.20
100	38.93
120	72.39
131.5	. 101.32



# TABLE 7-31 (cont.)

Latent Heat of Vaporization, kJ/mol	36.53
Viscosity, mPa.s 15 °C 30 °C 60 °C 120 °C 130 °C	0.844 0.711 0.512 0.313 0.292
C.A.S. Registry Number	108-90-7
Synonyms	Monochlorobenzene Phenyl chloride

# VAPOR PRESSURE-TEMPERATURE RELATIONSHIP

## FOR CHLOROBENZENE

TEMPERATURE, °C	VAPOR PRESSURE, kPa
0	0.40
20	1.20
40	3.47
60	8.67
80	19.20
100	38.93
120	72.39
131.5	101.32

# AZEOTROPES OF CHLOROBENZENE

OTHER COMPONENTS	B.PT. OF AZEOTROPE °C	CHLOROBENZENE wt %	WATER wt %	HYDROGEN CHLORIDE wt %
BINARY				*
Water	90.2	71.6	28.4	ž.
l-amino-2-propanol	128.3	87.0		
3-methyl-l-butanol	123.9	71.1		
2-methyl-l-butanol	124.4	57.0		,
n-propanol	96.5	20.0		
TERNARY				
Hydrogen chloride and water	96.9	74.5	20.2	5.3



Chlorobenzene is unaffected by steam, alkalis, hydrochloric acid or dilute sulfuric acid at moderate temperatures, and is unaffected by boiling for several hours with alcoholic potassium hydroxide solution.

The conversion of chlorobenzene to phenol by hydrolysis with steam requires temperatures of 450-500 °C in the presence of a catalyst. This hydrolysis can also be affected by alcoholic alkali solutions and water under pressure at high temperatures.

Chlorobenzene is reduced by hydrogen in the presence of reduced nickel at 270 °C to yield a mixture of benzene, biphenyl and hydrogen chloride.

Concentrated aqueous ammonia reacts with chlorobenzene, under pressure over a copper catalyst, to yield aniline. Anhydrous ammonia does not react with chlorobenzene.

Chlorobenzene reacts with hot concentrated sulfuric acid to give chlorobenzene-para-sulfonic acid.

On reaction of chlorobenzene with nitric acid at -30 to 0 °C, three chloronitrobenzene isomers are produced, the para-isomer predominating, and the meta-isomer being about 0.3 % of the total products. In the presence of mercury or mercury-silver amalgam, warm 50 % nitric acid reacts with chlorobenzene to yield chloronitrophenol and picric acid.

Chlorination of chlorobenzene in the presence of aluminium amalgam produces a mixture of ortho- and para-dichlorobenzenes, and a trace of the meta-isomer. Ferric and aluminium chlorides also catalyse this reaction. Chlorination in sunlight, in the absence of a catalyst, produces a mixture of chlorine addition compounds, eg octachlorocyclohexane.

When heated with bromine, chlorobenzene yields p-bromochlorobenzene as the principal product. Chlorobenzene reacts only slowly with iodine; after heating with iodine and sulfuric acid for several days, a mixture of p-chloroiodobenzene, 4-chloro-1,3-diiodobenzene, and chlorotriiodobenzene is formed.

Chlorobenzene reacts with sodium and sodium amalgam in the presence of boiling ethanol to form biphenyl.

Chlorobenzene reacts with carbon monoxide and hydrogen chloride, at elevated pressure and high temperature, to form p-chlorobenzaldehyde.

Potassium ferricyanide reacts with chlorobenzene at around 400 °C to form benzonitrile, an intermediate in dye syntheses.

Condensation of chlorobenzene with chloral in the presence of fuming sulfuric acid yields dichlorodiphenyltrichloroethane (DDT).

### 7.15 DICHLOROBENZENES

#### 7.15.1 INTRODUCTION

There are three isomers of dichlorobenzene; ortho-dichlorobenzene (1,2-dichlorobenzene), meta-dichlorobenzene (1,3-dichlorobenzene) and para-dichlorobenzene (1,4-dichlorobenzene). Ortho- and meta-dichlorobenzene are both mobile, colorless liquids with characteristic aromatic odors. Para-dichlorobenzene is a white crystalline solid with a penetrating camphor-like odor.

Ortho-dichlorobenzene is used in the manufacture of dye intermediates and as a special purpose solvent. It has minor application as an insecticide. Para-dichlorobenzene is used principally as a moth repellant and in deodorant formulations. Meta-dichlorobenzene is of no commercial interest at the present time.

All three isomers are produced by chlorination of benzene or chlorobenzene.

Cohen and Hartley, in 1905, investigated the progressive chlorination of benzene, using aluminium amalgam as catalyst. In 1920, Bour on, and, in 1948, MacMullin, on the basis of experimentally determined reaction rates and certain simplifying assumptions, derived equations for the distribution of products in benzene colorination. Ortho- and meta-dichlorobenzene have been known since 1875; the para-isomer was described by Muller in 1864.

## 7.15.2 PHYSICAL PROPERTIES

The physical properties of the dichlorobenzene isomers are listed

in Table 7-34 (1, 2, 3), and their vapor pressure-temperature relationships are presented in Table 7-35 (3).

The solvent behaviour of ortho-and meta-dichlorobenzenes closely resembles that of chlorobenzene (see Section 7.14.2).

Ortho-dichlorobenzene forms fourteen binary azeotropes, and paradichlorobenzene forms twenty. The azeotropic behaviour of metadichlorobenzene has not been reported.

Para-dichlorobenzene crystals sublime at ordinary temperatures, and are soluble in most organic solvents. The para-isomer forms a eutectic mixture (mp, -24.4 °C) with 86 % ortho-isomer.

#### 7.15.3 CHEMICAL PROPERTIES

In substitution reactions of aromatic compounds, the chlorine atom is ortho- and para-directing and deactivates the ring towards further substitution. Thus the dichlorobenzenes follow the general chemistry of other benzene derivatives, but react only under vigorous conditions.

Chlorination requires the presence of a catalyst, usually aluminium amalgam. All three dichlorobenzene isomers yield principally 1,2,4-trichlorobenzene.

Nitration of the dichlorobenzene isomers with strong nitric acid yields different products. The ortho-isomer yields principally 3,4-dichloro-l-nitrobenzene; the meta-isomer yields mainly 2,4-dichloro-l-nitrobenzene; and the para-isomer yields mainly 2,5-dichloro-l-nitrobenzene. With fuming nitric acid, ortho-dichlorobenzene gives 4,5-dichloro-l,2-dinitro-benzene, and para-dichlorobenzene gives 2,5-dichloro-l,3-dinitrobenzene.

TABLE 7-34

# PHYSICAL PROPERTIES OF THE

# DICHLOROBENZENE ISOMERS

PROPERTY	ORTHO-	META-	PARA-
Molecular Formula			
Physical State	liquid	liquid	solid
Molecular Weight	147.01	147.01	147.01
Melting Point, °C	-17.0	-24.7	53.1
Boiling Point, "C	180.5	173	174
Density, 20 °C, g/cm <sup>3</sup>	1.3048	1.2884	1.2475
Refractive Index, n <sup>20</sup> <sub>D</sub>	1.5515	1.5459	1.5285
Latent Heat of Vaporization, J/g Latent Heat of Fusion, J/g	269.9	-	-
Latent Heat of Fusion, J/g	87.95	85.98	124.14
Specific Heat, J/g, °C	1.126	1.126	1.243
Dielectric Constant, 25 °C	6.8281	-	-
C.A.S. Registry Number *	95-50-1	541-73-1	106-46-7
Synonyms	1,2-dichloro- benzene Dowtherm E	l,3-dichloro- benzene	1,4-dichlord benzene Dichloricide Paramoth Santochlor

<sup>\*</sup> C.A.S. Registery Number for dichlorobenzene (isomer unspecified) is 25321-22-6

TABLE 7-35

VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS

FOR THE DICHLOROBENZENE ISOMERS

VAPOR PRESSURE, kPa	TEMPERATURE, °C		
	ORTHO-	META -	PARA-
0.133	20.0	12.1	-
0.667	46.0	39.0	-
1.333	59.1	52.0	54.8
2.666	73.4	66.2	69.2
5.333	89.4	82.0	84.8
7.999	99.5	92.2	95.2
13.332	112.9	105.0	108.4
26.665	133.4	125.9	128.3
53.330	155.8	149.0	150.2
101.325	180.5	173.0	173.9

Ortho-dichlorobenzene reacts readily with fuming sulfuric acid, yielding 3,4-dichlorobenzene-l-sulfonic acid. The meta-isomer yields 2,4-dichlorobenzene-l-sulfonic acid, and the para-isomer gives, on sulfonation with sulfur trioxide vapor, 2,5-dichlorobenzene-l-sulfonic acid.

At moderate temperatures, ortho-dichlorobenzene is resistant to alkaline hydrolysis. However, it reacts in the presence of copper salts and about 200 °C to give ortho-chlorophenol; with alcoholic ammonia at 200 °C, o-chloroaniline is produced.

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8 MAJOR PRODUCERS, PRODUCTS AND USES



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#### 8.1 SUMMARY

The available literature on the production, uses and market forecasts for selected chlorinated hydrocarbons has been reviewed and discussed.

Information of this type for these compounds is very limited. The reason for this is that there are only one or two manufacturers for these compounds in Canada, thus Statistics Canada (a primary data source) does not release figures on production and uses for confidentiality reasons.

Only some of these chlorinated hydrocarbons are manufactured in Ontario. These are carbon tetrachloride, ethylene dichloride (1,2-dichloroethane), 1,1,1-trichloroethane, tetrachloroethylene (perchloroethylene), and possibly chloroform. Chlorinated hydrocarbons which are used in Ontario, but not manufactured (although some purification facilities may exist), are methyl chloride, methylene chloride, trichloroethylene, chlorobenzene, and o- and p-dichlorobenzene. 1,1-dichloroethane, 1,1,2-trichloroethane, and the tetrachloroethanes are not manufactured or used in Ontario or Canada, but may occur as captive intermediates or by-products in the synthesis of other chlorinated hydrocarbons. Chloroprene and vinylidene chloride (1,1-dichloroethylene) are not manufactured in Ontario or Canada, and are only imported and used in polymer from, ie vinylidene resins and polychloroprene (neoprene).

The general use of most of these chlorinated hydrocarbons is as solvents. Exceptions are chloroform and carbon tetrachloride, which are primarily used to manufacture chlorofluoromethanes, 1,2-dichloroethane (ethylene dichloride) which is mainly used as an intermediate in the

manufacture of vinyl chloride monomer, and methyl chloride which is mainly used in the manufacture of tetramethyllead, methyl cellulose, and quaternary ammonium compounds.

Each of the other chlorinated hydrocarbons has one major use.

Methylene chloride has major use as a solvent in paint stripper formulations,

1,1,1-trichloroethane (methyl chloroform) is used as a cold and vapor

degreasing solvent, trichloroethylene is used as a vapor degreasing solvent,

perchloroethylene is used as a dry-cleaning solvent. Chlorobenzene is

only used in small quantities as a specialty solvent. Ortho-dichlorobenzene

is also only used in small quantities, mainly as a solvent in rust

removal and prevention formulations. Para-dichlorobenzene is used as a

deodorant and moth repellant.

The only chlorinated hydrocarbons whose use is expected to grow significantly over the next few years are 1,2-dichloroethane (for vinyl chloride manufacture), methylene chloride, 1,1,1-trichloroethane, and perchloroethylene.

#### 8.2 INTRODUCTION

Chlorinated hydrocarbons occupy an important place in the economy of the chemical industry. They provide the principal routes by which chlorine reaches the chemical market. Thus, the chlorinated hydrocarbons are the most important link between the inorganic and organic chemical industries.

Their development began in the early 1860's and was accelerated in the years following World War I by the emergence of liquified chlorine as the principal commercial chlorine commodity, displacing bleaching powder, which had held this position for almost a century. During and after World War II, chlorinated hydrocarbons manufacture and usage developed rapidly, along with the development of the organic chemical industry, and in particular, with the huge expansion of the petrochemical industry.

The by-product hydrogen chloride from hydrocarbon chlorination is being used to an increasing extent in the production of further chlorinated organic derivatives, either by oxidation to recover chlorine, or by its reaction with ethylene, and, to a lesser extent, acetylene (hydrochlorination).

The interest in chlorinated hydrocarbons is principally due to their tremendous solvent power for organic, and a large number of inorganic, materials. While other organic compounds are good general solvents, few equal the chlorinated hydrocarbons in this respect.

Some chlorinated hydrocarbons are of principal interest as raw materials in other manufacturing processes. For example, chloroform

and carbon tetrachloride are mainly used to manufacture chlorofluoromethanes, which are important as refrigerants and aerosol propellants. 1,2-dichloroethane (ethylene dichloride) is used to manufacture vinyl chloride, a very important monomer in plastics manufacturing. Other chlorinated hydrocarbons used in polymer formulations are vinylidene chloride (1,1-dichloroethylene) and chloroprene.

However, apart from 1,2-dichloroethane and carbon tetrachloride, the major interest in chlorinated hydrocarbons in Ontario is from their use as solvents.

## 8.3 METHYL CHLORIDE

## 8.3.1 INTRODUCTION

Methyl chloride ( $\mathrm{CH_3^{Cl}}$ ), at ambient temperature and pressure, is a colorless gas with an ethereal odor and a sweetish taste. Commercially, methyl chloride is handled in the liquified form.

The major uses of methyl chloride are in the manufacture of silicones, tetramethyllead, synthetic rubber, methyl cellulose and as a methylating agent. It is also used in aerosol propellant formulations, and as a blowing agent in foamed plastics manufacture. Some methyl chloride may still be used in grain fumigant formulations, but this practice has largely been discontinued.

Methyl chloride is manufactured by two processes, these are by chlorination of methane, and by reaction of hydrogen chloride with methanol. The former process is the principal route to methyl chloride produced today.

Historically, the first uses of methyl chloride were as a refrigerant and in the synthesis of dyes. As long as methyl chloride demand was small, it could be supplied by the process, originated around 1875, of thermally decomposing betaine, recovered from waste materials of the sugar beet industry (1). Large-scale production began in the U.S. about 1920 chiefly to supply refrigerant requirements. From 1943 its production was greatly increased because of demand for its use as a starting material for the manufacture of methyl silicones and for use as a catalyst solvent in the manufacture of synthetic butyl rubber.

#### 8.3.2 PRODUCTION AND SOURCES

Methyl chloride is produced commercially from two processes:
by the reaction of hydrogen chloride with methanol, and by chlorination of methane. The methanol-hydrogen chloride reaction yields methyl chloride as the sole product, while chlorination of methane yields other chloromethanes as by-products. The co-products from chlorination of methane (methylene chloride, chloroform and carbon tetrachloride) are commercially important and thus methane chlorination can be regarded as a multiple product process. This process is the major commercial route to methyl chloride. A typical reaction product yields on fractionation 35 wt % methyl chloride, 45 wt % of methylene chloride and 20 wt % of chloroform plus carbon tetrachloride. However, by appropriate process control the product can be varied from almost 100 % methyl chloride to 100 % carbon tetrachloride.

Methyl chloride is not currently manufactured in Ontario or Canada.

Methyl chloride used in Ontario is imported and marketed by the Dow

Chemical Co. Ltd. in Sarnia.

#### 8.3.3 USES OF METHYL CHLORIDE

The amount of methyl chloride used and imported in Canada (as reported by Statistics Canada) is presented in Table 8-1. Manufacturers of industrial chemicals (organic) are the only industrial category reported as using methyl chloride.

Since there is no reported manufacture of methyl chloride in Canada, there appears to be a discrepancy between the amounts used and

TABLE 8-1

INDUSTRIAL USAGE AND IMPORTS OF METHYL CHLORIDE

(All figures in Gg/annum)

INDUSTRY	1973	1974	1975	1976	REF.
Manufacturers of Industrial Chemicals (organic) (SIC 3783)	7.38	6.30	7.58	n.a.	2
Amounts Imported	n.a.	2.93	3.08	3.47	3

n.a. = figures not available



amounts imported. A probable explanation is that Dow also imports a mixture of methyl and methylene chlorides for separation and purification (4). Such a mixture would be reported by Statistics Canada as imports under the classification "derivatives of hydrocarbons not elswhere specified" (406-99) (3).

Methyl chloride is used mainly as a blowing agent in foamed plastics manufacture (eg styrofoam - Dow Chemical Co.), in the manufacture of methyl- and carboxy-methyl-cellulose (Celanese Canada Ltd., Chemical Developments of Canada Ltd.), as a catalyst solvent in butyl rubber manufacture (Polysar Ltd.), and in the manufacture of tetramethyllead (Ethyl Corp., DuPont of Canada Ltd.). Methyl chloride is not used to manufacture silicones in Canada. Uses of methyl chloride as a refrigerant and grain fumigant are of minor importance.

#### 8.3.4 MARKET FORECAST

Insufficient data are available on the usage of methyl chloride in Ontario to allow prediction of market trends.

## 8.4 METHYLENE CHLORIDE

## 8.4.1 INTRODUCTION

Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), is a colorless, heavy, mobile liquid with a pleasant ethereal odor. It is the least toxic of the chloromethanes. The outstanding solvent properties of methylene chloride are the basis of its principal industrial uses.

The major use of methylene chloride is in paint stripper formulations. It is also used in solvent degreasing operations, in aerosol formulations, in the production of photographic film and synthetic fibres, and as an extractant in certain applications within the food processing industry.

Methylene chloride became an industrial chemical of importance during World War II, and since that time, production of this chemical has increased rapidly. This rapid expansion has been caused mainly by demand for methylene chloride for use in paint stripper formulations.

### 8.4.2 PRODUCTION AND SOURCES

Manufacturing processes for methylene chloride are based on the chlorination of methane or methyl chloride. The other chloromethanes are also produced as co-products of this process. However, by appropriate choice of conditions, methylene chloride can be obtained as the major product.

Methylene chloride is not manufactured in Ontario or Canada at the present time. Dow Chemical Co. Ltd. in Sarnia imports crude methylene chloride for purification and marketing.

#### 8.4.3 USES OF METHYLENE CHLORIDE

The amounts of methylene chloride used and imported in Canada as reported by Statistics Canada are presented in Table 8-2. Paint and varnish manufacturers are the only industrial category reported as using methylene chloride. Use in this industry is probably all in paint and varnish remover formulations. Figures for imports of methylene chloride are only available for 1976. Previously, data were reported under a general classification of "halogenated derivatives of hydrocarbons". Data for 1977 are not yet available.

Methylene chloride is used extensively in paint stripping and cold degreasing formulations because of its superior solvent properties. In these operations essentially all of the methylene chloride is eventually lost to the atmosphere. A common formulation for this application uses a mixture of methylene chloride and cresylic acids (a mixture of phenolic compounds) with a small amount of anionic surfactant. A layer of water is put over the mixture to reduce methylene chloride evaporation and odors from the cresylic acids.

Methylene chloride is also used as a vapor degreaser. In this application most of the solvent is recovered by condensation and adsorption, but some may still be lost. An inhibited form of methylene chloride has recently been introduced to the vapor degreasing market, and is claimed to be superior to the traditional solvents for this application (trichloroethylene and 1,1,1-trichloroethane). The inhibitor vaporizes close to the boiling point of methylene chloride (40 °C), and

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TABLE 8-2

## AMOUNTS OF METHYLENE CHLORIDE USED AND

# IMPORTED TO CANADA

(All figures in Gg/annum)

INDUSTRY	1973	1974	1975	1976	REF.
Paint and Varnish Manufacturers (SIC 375)	1.12	1.13	n.a.	n.a.	5
Amount Imported	n.r.	n.r.	n.r.	10.12	3

n.a. = figures not available

n.r. = figures not reported

so is able to inhibit the formation of hydrogen chloride even in the vapor phase (6).

This application of methylene chloride, if widely adopted, could become a major use for this chemical, particularly in view of concern about the occupational safety of trichloroethylene use.

Other uses of methylene chloride are in aerosol formulations; in the extraction of heat-sensitive substances in food processing such as edible fats, cocea butter, and the beer flavoring in hops; in the manufacture of photographic film where it is used as a polymer solvent; as a solvent for cellulose triacetate in rayon yarn manufacture; in the production of PVC fiber; and as a low temperature heat transfer medium. Methylene chloride is also used to clean reactors producing polyurethane (possible user is Uniroyal Ltd. in Elmira).

# 8.4.4 MARKET FORECAST

Because of the versatility and low toxicity of this solvent, it is expected that usage will grow, particularly in degreasing applications.

## 8.5 CHLOROFORM

## 8.5.1 INTRODUCTION

Chloroform (CHCl<sub>3</sub>) is a heavy, colorless, volatile liquid having a pleasant ethereal odor.

The major use of chloroform is as a raw material in the manufacture of chlorodifluoromethane (CHClF<sub>2</sub>), an important refrigerant and coolant for air conditioning systems. Chloroform is also used as an extractant for naturally occurring substances and in the manufacture of some pharmaceutical preparations. It has a wide but relatively minor use as a solvent.

Historically, interest in chloroform began with its use as an anaesthetic. Large scale production of chloroform was begun in the U.S. in 1869 by the Pennsylvania Salt Manufacturing Co. In 1903, the Midland Chemical Co., a subsidiary of Dow Chemical Co., began manufacture of chloroform by reduction of carbon tetrachloride. Chloroform was one of the first organic chemicals produced on a large scale in the U.S. (1).

Immediately prior to World War II in the U.S., chloroform was still being used mainly as an anaesthetic and in pharmaceutical preparations. During World War II chloroform production increased threefold, largely to meet requirements for penicillin manufacture, where it was used as an extractant. After the war, demand for chloroform continued to increase as its technical applications were extended. Today most chloroform is used in the manufacture of chlorodifluoromethane, with pharmaceutical uses being of only minor importance.

#### 8.5.2 PRODUCTION AND SOURCES

A large number of compounds, containing either the CH<sub>3</sub>CC- or CH<sub>3</sub>CH(OH)-group, yield chloroform on reaction with chlorine and alkali. Until around 1960, chloroform was made almost exclusively from acetone or ethanol by this reaction. The principal process in use today is chlorination of methane. The chlorination of methane yields a mixture of chloromethanes. However, by appropriate modifications and choice of process conditions, chloroform can be obtained as the principal product.

In 1975 the only reported manufacturer of chloroform in Canada was Canadian Industries Ltd. (7), who produced this chemical at their Shawinigan, Quebec, plant. It is not certain whether this production still continues. Dow Chemical Co. of Sarnia, Ontario import chloroform for their own use and for distribution.

#### 8.5.3 USES OF CHLOROFORM

The only figures released by Statistics Canada on chloroform are the amounts imported. Imports for 1974-76 are 0.47, 2.77 and 2.77 Gg for each year respectively (3).

It is not certain whether C.I.L. still manufactures chloroform in Canada. No figures are available for the chloroform production capacity of C.I.L.'s Shawinigan plant.

Both DuPont Ltd. in Maitland and Allied Chemical Ltd. in Amherstburg use chloroform to manufacture chlorodifluoromethane (8). This chemical is used as a refrigerant and is also used (in the U.S.) as in intermediate for tetrafluoroethylene manufacture.

Dow Chemical Ltd. in Sarnia import chloroform as a feedstock and for marketing. Dow likely uses chloroform as a solvent in specialty formulations (eg fumigants, insecticides and fungicides).

Other uses of chloroform are in liquid pharmaceutical preparations (eg analgesics, anthelmintics, carminatives, expectorants and liniments), in toothpaste formulations as a taste enhancer, and as an extractant for naturally occurring substances, such as penicillin, essential oils and alkaloids.

Use of chloroform as an anaesthetic has largely been discontinued.

### 8.5.4 MARKET FORECAST

With the reduction in the use of chlorofluoromethanes, it is expected that chloroform usage for manufacture of these compounds will remain constant or decrease.

Current concern about possible carcinogenic effects of chloroform indicates that its use in pharmaceutical preparations and toothpastes may be severely curtailed, or banned.

## 8.6 CARBON TETRACHLORIDE

## 8.6.1 INTRODUCTION

Carbon tetrachloride ( $CCl_4$ ) is a heavy, colorless, nonflammable liquid with a characteristic, non-irritant odor. It is the most toxic of the chloromethanes. Thermal oxidation yields phosgene and other toxic products.

The principal use of carbon tetrachloride is in the manufacture of chlorofluoromethanes. Other uses are as a fire extinguishing fluid, as a grain fumigant, and as a solvent.

In the 1890's, processes for the commercial manufacture of carbon tetrachloride first appeared in Europe. Production of carbon tetrachloride on a large scale began in the U.S. about 1907 for use in dry-cleaning and for fire extinguishers. During World War I, U.S. production of carbon tetrachloride greatly expanded, and its use was extended to grain fumigation and the rubber industry. World War II also stimulated carbon tetrachloride manufacture, and marked the beginning of its most important present-day use, as a feedstock for chlorofluoromethanes manufacture (1).

#### 8.6.2 PRODUCTION AND SOURCES

Carbon tetrachloride can be made by two processes; the chlorination of carbon disulfide, and the chlorination of hydrocarbons. The latter process is by far the most important today, and is the one used to manufacture carbon tetrachloride in Canada.

There are currently two producers of carbon tetrachloride in Canada, both plants being located in Ontario. These are Dow Chemical Ltd. in

Sarnia who produce carbon tetrachloride and co-product perchloroethylene by the chlorination of propane, and Canadian Industries Ltd. who produce carbon tetrachloride at their subsidiary Cornwall Chemicals plant in Cornwall. Capacity at the Dow Chemical plant is estimated as 30 Gg/annum of combined carbon tetrachloride/perchloroethylene (4). It is difficult to obtain separate figures for these two chemicals, as Dow's facility can adjust its operation to produce one or the other chemical in greater yield depending upon market demands (4). The Cornwall chemicals plant has an estimated capacity of 20 Gg/annum (4).

Import figures for carbon tetrachloride are only available for 1976 (3), and show that 0.35 Gg were imported, all from the U.S.

## 8.6.3 USES OF CARBON TETRACHLORIDE

The amounts of carbon tetrachloride used by various industries as reported by Statistics Canada are presented in Table 8-3.

Use of carbon tetrachloride by manufacturers of industrial chemicals (inorganic) is by production of chlorofluoromethanes by Allied Chemical at Amherstburg, Ontario, who receive shipments from Dow. Use of carbon tetrachloride by manufacturers of industrial chemicals (organic) is also for production of chlorofluoromethanes, but by DuPont of Canada Ltd., of Cornwall, Ontario, who receive shipments from Cornwall Chemicals (C.I.L.). However, this figure includes uses of carbon tetrachloride by Dow Chemical for various proprietary formulations, particularly in grain fumigants. Carbon tetrachloride is used as a grain fumigant in combination with ethylene dibromide and ethylene dichloride,

TABLE 8-3

AMOUNTS OF CARBON TETRACHLORIDE

USED BY INDUSTRY

INDUSTRY	1973	1974	1975	REF.
Manufacturers of Industrial Chemicals (inorganic) (SIC3972)	0 02 0-	12.00.0		
Manufacturers of Industrial	8.83 Gg	13.29 Gg	n.a.	2
Chemicals (organic) (SIC 3873)	14.68 Gg	16.95 Gg	n.a.	2
Miscellaneous Chemical Industries		_		
(SIC 379)	n.a.	5.91 Mg	5.00 Mg	9



n.a. = figures not available

where, apart from its toxic effects, it assists in downward penetration through the grain container of the other more toxic constituents of the formulation.

The reason for the amounts of carbon tetrachloride used as a raw material for chlorofluoromethanes (CFM) manufacture being reported in two separate categories (inorganic and organic chemicals manufacture) is because of the nature of the plants making CFMs. Allied Chemical's plant at Amherstburg manufactures predominantly inorganic chemicals, CFMs being the only organic chemicals manufactured there (7). Thus, usage of carbon tetrachloride at this plant appears under "manufacturers of industrial chemicals (inorganic)". DuPont of Canada Ltd.'s plant at Maitland manufactures predominantly organic chemicals (7), and usage of carbon tetrachloride by this plant appears under "manufacturers of industrial chemicals (organic)".

Uses of carbon tetrachloride by miscellaneous chemical industries is probably in speciality solvent applications. Carbon tetrachloride is also used in fire extinguishers.

## 8.6.4 MARKET FORECAST

Because of the reduction in the use of chlorofluoromethanes as aerosol propellants, the production of carbon tetrachloride is expected to drop from its current level of around 35 Gg/annum to about 25-30 Gg/annum by 1980 (4). Other uses of carbon tetrachloride are expected to increase by a small percentage, but these uses are minor compared to chlorofluoromethane production.

## 8.7 ETHYLENE DICHLORIDE (1,2-DICHLOROETHANE)

#### 8.7.1 INTRODUCTION

1,2-dichloroethane,  $CH_2CICH_2CI$ , is a colorless liquid with an odor resembling that of chloroform.

The principal use of 1,2-dichloroethane is as an intermediate in the manufacture of vinyl chloride. It is also used as a raw material for manufacture of 1,1,1-trichloroethane. Other uses are as a constituent of tetraethyl lead gasoline additives, and in fumigant formulations. It has been used as a solvent.

## 8.7.2 PRODUCTION AND USES

Production of 1,2-dichloroethane is by reaction of chlorine with ethylene in the presence of a catalyst. The process is usually carried out in the gas phase. The 1,2-dichloroethane product is condensed and purified by fractional distillation.

There are two producers of 1,2-dichloroethane in Ontario. These are Dow Chemical of Canada Ltd. in Sarnia and Ethyl Corporation Ltd. in Corunna. Dow is by far the largest producer with estimated capacity of 135-180 Gg/annum, and uses most of the 1,2-dichloroethane in a captive process to manufacture vinyl chloride monomer. Ethyl Corporation manufactures a small amount of 1,2-dichloroethane for use as an additive in tetraethyllead formulations. 1,2-dichloroethane is added at a level of about 10 % of the tetraethyllead, and acts as a lead scavenger in internal combustion engines by formation of volatile lead chloride. Tetraethyllead additives are added to gasoline as an antiknock agent.

Statistics Canada (10) reports the use of 42.0 Gg of tetraethyl fluid in 1974, and 42.79 Gg in 1975. This would correspond to about 5 Gg of 1,2-dichloroethane being used for this purpose in these years.

1,2-dichloroethane is also used in grain fumigant formulations, usually in admixture with carbon tetrachloride and ethylene dibromide.

These formulations are produced by Dow Chemical of Canada Ltd.

A further use of 1,2-dichloroethane is in the manufacture of 1,1,1-trichloroethane. About 10-15 Gg of 1,1,1-trichloroethane are produced by Dow Chemical, which would require about 6.5-10 Gg/annum of 1,2-dichloroethane (assuming around 90 % conversion).

Statistics Canada (3) reports that 0.11 Gg of 1,2-dichloroethane were imported to Canada in 1976.

## 8.7.3 MARKET FORECAST

The key factors in the growth of 1,2-dichloroethane production are the growth of the domestic polyvinyl chloride (PVC) market, and the ability to export 1,2-dichloroethane, vinyl chloride, and/or PVC resin.

Current capacity for 1,2-dichloroethane production is 135-180 Gg/annum. However, Dow Chemical of Canada Ltd. is building a world-scale 1,2-dichloroethane to vinyl chloride monomer plant (around 650 Gg/annum) at Fort Saskatchewan, Alberta to be completed by 1980. This will raise manufacturing capacity for 1,2-dichloroethane in Canada to around 800 Gg/annum.

Forecasts of Canadian consumption of 1,2-dichloroethane are 630 Gg/annum by 1980, 665 Gg/annum by 1985, and 950 Gg/annum by 1990, assuming

additional capacity of 320 Gg/annum by 1990. Most of this consumption will be in the manufacture of vinyl chloride for PVC production.

Use of 1,2-dichloroethane as an intermediate in 1,1,1-trichloroethane is expected to grow significantly, as 1,1,1-trichloroethane assumes more of the vapor-degreasing market. Production of 1,1,1-trichloroethane can be made an integral part of 1,2-dichloroethane and vinyl chloride manufacturing processes. Thus, production of this chemical can be linked directly to market demands.

The use of 1,2-dichloroethane in tetraethyllead and tetramethyllead gasoline additives is expected to decline, as leaded gasolines are phased out of the market.

Uses of 1,2-dichloroethane in fumigant formulations and in solvent applications will probably remain at about the same level.

# 8.8 TRICHLOROETHANE

## 8.8.1 INTRODUCTION

1,1,1-trichloroethane,  $CH_3CC1_3$ , is a colorless mobile liquid with a characteristic odor.

The principal uses of l,l,l-trichloroethane are as a metal degreaser and as an extracting solvent. Use of l,l,l-trichloroethane as a degreasing solvent and in several other solvent applications was begun in the 1950's; up to that time the compound had been of no commercial interest. Today, l,l,l-trichloroethane is displacing trichloroethylene as the principal metal degreasing solvent.

# 8.8.2 PRODUCTION AND USES

1,1,1-trichloroethane can be manufactured by a number of different routes. However, the process used in Canada is believed to be by chlorination of 1,2-dichloroethane. The co-product hydrogen chloride which is formed can be either collected for hydrochloric acid production, or recycled and reacted with vinyl chloride to produce further 1,2-dichloroethane.

The only manufacturer of 1,1,1-trichloroethane in Canada is Dow Chemical of Canada Ltd. of Sarnia, Ontario. Dow is also the only Canadian producer of vinyl chloride monomer, and the major producer of 1,2-dichloroethane. Dow's capacity for 1,1,1-trichloroethane is estimated to be 15-20 Gg/annum (4).

Statistics Canada lists no separate uses for 1,1,1-trichloroethane. However, the amount imported to Canada in 1976 was 0.52 Gg (3) which

indicates that Dow Chemical's production meets almost all of Canadian requirements at the present time.

The major use of 1,1,1-trichloroethane is as a vapor degreaser.

In this application it is winning more of the market from trichloroethylene.

1,1,1-trichloroethane is also used as a cold cleaning solvent,
particularly for electrical machinery components.

Other uses are as a solvent in contact cements, rubber cements, and in some paints. This use is expected to increase (8).

## 8.8.3 MARKET FORECAST

Because of concern over possible carcinogen effects of trichloroethylene, 1,1,1-trichloroethane is expected to become the major solvent used in vapor degreasing operations. Usage is currently growing at around 10 % per year (4).

# 8.9 <u>TETRACHLOROETHANE</u>

## 8.9.1 INTRODUCTION

1,1,2,2-tetrachloroethane,  $\mathrm{CHCl}_2\mathrm{CHCl}_2$ , is a dense, colorless, nonflammable liquid with a heavy sweet odor.

The only significant use of 1,1,2,2-tetrachloroethane is as an intermediate in the manufacture of trichloroethylene and tetrachloroethylene from acetylene. The other uses of this compound are of very minor importance, and are usually discouraged because of its high toxicity. These applications are as an insecticide and a special-purpose solvent.

# 8.9.2 PRODUCTION AND USES

1,1,2,2-tetrachloroethane is manufactured by chlorination of acetylene, in the presence of diluents and a catalyst, usually ferric chloride. It can also be made by chlorination of 1,2-dichloroethylene.

1,1,2,2-tetrachloroethane is only produced in Canada as a captive intermediate in the manufacture of trichloroethylene and perchloroethylene. The only company using this process is Canadian Industries Ltd. (C.I.L.) at their Shawinigan, Quebec plant.

Statistics Canada reports no uses or imports of 1,1,2,2-tetrachloroethane to Canada.

Applications of tetrachloroethane, apart from as an intermediate, are in fumigant formulations and as a specialty solvent, as, for example, in the extraction of ruthenium, chlorinated phthalic anhydride, sulphur, and sodium sulphite. It is believed that no 1,1,2,2-tetrachloroethane is used for these purposes in Ontario or Canada.

## 8.10 DICHLOROETHYLENE

## 8.10.1 INTRODUCTION

1,1-dichloroethylene (vinylidene chloride),  $\mathrm{CH}_2=\mathrm{CCl}_2$ , is a clear, mobile, volatile liquid with a sweetish odor. The commercial importance of 1,1-dichloroethylene is almost entirely due to its use as a polymer, and in the manufacture of co-polymeric materials with monomers such as vinyl chloride, acrylonitrile and methyl methacrylate.

# 8.10.2 PRODUCTION AND USES

1,1-dichloroethylene is produced by dehydrochlorination of 1,1,2-trichloroethane by agitating with an aqueous suspension of calcium hydroxide at around 50 °C. The 1,1-dichloroethylene is distilled off as it forms and purified by further distillation.

Purified 1,1-dichloroethylene is generally polymerized within a short time after its production, as it slowly polymerizes on long term storage, and also forms peroxides on exposure to air.

There is no production of 1,1-dichloroethylene in Canada at the present time, and none of this compound is imported as the monomer.

Statistics Canada does not list any separate uses of vinylidene chloride resins. Imports of vinylidene resins (which include polymer resins prepared with vinylidene chloride) were 3.09, 1.79 and 2.33 Gg for 1974-76 respectively (3).

Vinylidene chloride co-polymers are used in the production of such articles as gasoline filters, valves, pipe fittings, containers, and chemical process equipment, where chemical resistance and extended service

life are required. They are also used as lacquer resins, as barrier coatings on paper products, and in the production of plastic film (Saran-wrap).

## 8.10.3 MARKET FORECAST

It is unlikely that vinylidene chloride will be produced in Canada.

Its polymer usage is fairly small and does not warrant the establishment of a domestic manufacturing facility.

# 8.11 TRICHLOROETHYLENE

## 8.11.1 INTRODUCTION

Trichloroethylene,  $CHCl=CCl_2$ , is a colorless, volatile liquid with a sweet odor. It is a powerful solvent for a large number of natural and synthetic organic substances.

The main use of trichloroethylene is as a vapor degreasing solvent.

It is sometimes used as a cold degreasing and dry-cleaning solvent.

Minor applications are as an extractant for naturally occurring substances, such as waxes and greases from cotton and wool, and caffeige from coffee beans. It has also been used as a low temperature heat-transfer medium and as a component of rust prevention formulations.

Production of trichloroethylene first began in 1908 in Austria as a chemical outlet for surplus acetylene. Production facilities in England and Germany soon followed; production in the U.S. began in 1925.

No systematic attempt was made to find a major outlet for trichloroethylene until the late 1920's when the invention of efficient metal degreasing units and the spread of dry-cleaning establishments provided a basis for production growth. By 1950 trichloroethylene had displaced carbon tetrachloride as a dry-cleaning solvent, and was itself later displaced by perchloroethylene in this application (1). Its principal application today is as a metal degreaser.

# 8.11.2 PRODUCTION AND USES

Trichloroethylene is manufactured from 1,1,2,2-tetrachloroethane, which is itself manufactured from acetylene. Dehydrochlorination of 1,1,2,2-tetrachloroethane to trichloroethylene can be carried out using

two types of processes: treatment with aqueous alkali, and pyrolysis with or without catalysts.

All trichloroethylene produced in Canada is manufactured by Canadian Industries Ltd. (C.I.L.) at its Shawinigan, Quebec plant. Estimated capacity for trichloroethylene/perchloroethylene production is 15-25 Gg/annum (4, 11).

Table 8-4 presents amounts of trichloroethylene used by various industries and amounts imported as reported by Statistics Canada. The use of trichloroethylene in these industries is as a solvent and extractant.

Total Canadian consumption of trichloroethylene is estimated to be 16-18 Gg/annum (11). Most of this consumption is as a vapor degreasing solvent. There are estimated to be 2000-3000 vapor degreasing units in Ontario alone, ranging from very small operations (eg parts cleaning in garages) to large degreasers in the major metal fabricating industries (8).

Trichloroethylene is also used to extract naturally occurring substances. For example, it is used to extract caffeine from coffee beans prior to production of decaffeinated coffees (12), to extract oils and waxes from fish proteins, in the production of spice oleoresins, and to extract cocoa butter from cocoa beans.

Trichloroethylene has been used as an inhalation analgesic and anaesthetic.

UNITED TECHNOLOGY and SCIENCE INC.

AMOUNTS OF TRICHLOROETHYLENE IMPORTED AND AMOUNTS

USED BY VARIOUS INDUSTRIES

	1973	1974	1975	1976	REF.
Imports	n.a.	1.04 Gg	<b>3.</b> 95 Gg	1.06 Gg	3
Paint and Varnish Manufacturers (SIC 375)	19.4 Mg	55.3 Mg	n.a.	n.a.	. 5
Manufacturers of Soaps and Cleaning Compounds (SIC 376)	n.a.	20.5 Mg	8.9 Mg	n.a.	13
Miscellaneous Chemical Industries (SIC 376)	n.a.	0.46 Gg	0.26 Gg	n.a.	9



n.a. = figures not available

#### 8.11.3 MARKET FORECAST

Demand for trichloroethylene is expected to decline, as 1,1,1trichloroethane takes over more of the vapor degreasing market. This
substitution is because of concern over possible carcinogenic effects
of trichloroethylene, and suspected contribution of this compound to
photochemical smog formation.

A curtailment of the use of trichloroethylene as an extractant in food processing may also occur due to concern over its carcinogenic effects.

A second manufacturer of trichloroethylene in Canada was VenChem

Ltd. of Shawinigan, Quebec. This facility was launched by Alcan Ltd.

in 1975 to meet a predicted demand for trichloroethylene and perchlorotheylene
in Quebec and Eastern U.S., by using surplus chlorine from Alcan's Alvida,

Quebec plant and acetylene from Gulf Canada Ltd.'s calcium carbide plant
in Varennes, Quebec. However, the expected demand for these solvents did

not occur, and strikes at both raw materials plants caused curtailments
of VenChem's production. In mid-1976, closure of Alcan's chloralkali

plant caused trichloroethylene production at VenChem to be severely

reduced, and the plant was eventually closed down. Closure of this

facility ended prospects for significant exports of trichloroethylene (4).

## 8.12 PERCHLOROETHYLENE

#### 8.12.1 INTRODUCTION

Perchloroethylene (tetrachloroethylene),  $CCl_2 = CCl_2$ , is a clear, colorless, dense liquid with an ethereal odor. Tetrachloroethylene is a good solvent for a large number of organic compounds.

The principal use of perchloroethylene is as a dry-cleaning solvent. It is also used for metal degreasing and as a solvent for a number of organic materials such as fats, oils, tars, rubber, and gums, and in the synthesis of trichloroacetic acid. It has been used medically as a vermifuge (to expel parasitic worms).

Perchloroethylene was first produced around 1910 in the U.K. and Germany; production in the U.S. was not begun until 1925. Manufacture of perchloroethylene was integrated with trichloroethylene manufacture from the outset. In the 1930's, development of the small dry-cleaning units stimulated demand for the solvent in the U.S. Following World War II, tetrachloroethylene usage as a dry-cleaning solvent increased greatly (1).

#### 8.12.2 PRODUCTION AND USES

Tetrachloroethylene can be produced industrially by a number of processes. The most important processes are by dehydrochlorination of pentachloroethane, by chlorination-dehydrochlorination of 1,1,2,2-tetrachloroethane, and by chlorination of propane. The latter two processes are believed to be the manufacturing routes to perchloroethylene in Canada.

There are two producers of perchloroethylene in Canada, one being located in Ontario. These producers are Canadian Industries Ltd. (C.I.L.) at their Shawinigan, Quebec plant, and Dow Chemical of Canada Ltd. at Sarnia, Ontario. C.I.L. is believed to produce perchloroethylene from chlorination of acetylene with 1,1,2,2-tetrachloroethane as intermediate. Estimated capacity for perchloroethylene and trichloroethylene is 15-25 Gg/annum (4, 11). About 7 Gg/annum of this figure is estimated to be perchloroethylene. Dow Chemical is believed to manufacture perchloroethylene by chlorination of propane, carbon tetrachloride also being co-produced. Estimated capacity for perchloroethylene/carbon tetrachloride production is 30 Gg/annum (4). It is difficult to estimate the perchloroethylene part of this figure, as the process can be adjusted to give either product in greater yield depending upon market demands. The peak shipments of carbon tetrachloride from this plant for fluorocarbon manufacture occurred in 1974 at 13 Gg/annum (4), indicating that perchloroethylene production for that year was around 17 Gg/annum. production of perchloroethylene in Canada is estimated to be 20-25 Gg/ annum from these figures.

Statistics Canada lists no separate figures for industrial usage of perchloroethylene. However, imports were 1.45 Gg for 1976 (3).

The major use of perchloroethylene is as a dry-cleaning solvent.

There are probably several thousand dry-cleaning establishments in

Ontario, and usage of perchloroethylene in this application is generally distributed according to population density.

Other uses of perchloroethylene are as a metal degreasing solvent, in the extraction of fats, and other specialty solvent purposes. One special-purpose application is in the electro-winning plant of Inco Ltd., where hot perchloroethylene is circulated to remove sulfur (8).

## 8.12.3 MARKET FORECAST

Demand for perchloroethylene as a dry-cleaning solvent is expected to rise slowly (4). Other minor uses for perchloroethylene will probably remain constant. The closure of the VenChem facility at Shawinigan, Quebec (see Section 8.11.3), the third Canadian producer of perchloroethylene, essentially ends prospects of significant exports of perchloroethylene. However, a substantial upturn in demand for perchloroethylene and trichloroethylene could lead to this plant being reopened. This would add capacity for perchloroethylene/trichloroethylene production of 23 Gg/annum. The prospects for this plant reopening, however, do not look good at the present time.

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## 8.13 CHLOROPRENE

## 8.13.1 INTRODUCTION

Chloroprene (2-chloro-1,3-butadiene),  $CH_2$ = $C(C1)CH=CH_2$ , is a colorless, mobile liquid with a characteristic odor and has great reactivity.

Chloroprene is of commercial importance as the raw material for the manufacture of synthetic elastomers marketed under the generic name, neoprene.

The first manufacture of chloroprene in the 1930's started from monovinylacetylene, which was itself manufactured from acetylene. Other manufacturing processes for chloroprene, using butanes, butenes or butadienes as raw materials, have since been developed and are now the major production routes.

# 8.13.2 PRODUCTION AND USES

Chloroprene is produced by two processes. These processes are by the hydrochlorination of monovinylacetylene, and by the chlorination of butadiene followed by dehydrochlorination of the 3,4-dichloro-1-butene intermediate. The latter is the process by which chloroprene is manufactured today.

All chloroprene and polychloroprene produced in North America is manufactured by DuPont and Petrotex Chemical in the U.S. (14). No chloroprene or polychloroprene is manufactured in Canada (15).

Polychloroprene (neoprene) is obtained by emulsion polymerization of chloroprene and consists mainly of 1,4-trans-polychloroprene. Neoprene is resistant to weathering and oil. It is also resistant to abrasion, heat, flame, oxygen, ozone and solvents. The main applications of neoprene

are in high performance articles such as cable sheaths, hose, rubberized fabrics, adhesives, and a large number of technical rubber articles (1). The automotive industry is a large user of neoprene.

The amounts of polychloroprene used in the rubber products industry in Canada are 6.8, 6.1, 5.5 and 6.2 Gg for the years 1973 to 1976 respectively (16). Statistics Canada (9) reports the use of 0.78 Gg and 0.74 Gg of neoprene in 1974 and 1975 respectively, this neoprene being used to manufacture 4.49 G1 (1974) and 5.15 M1 (1975) of rubber adhesives.

# 8.13.3 MARKET FORECAST

It is not known whether a chloroprene manufacturing facility will be established in Canada. However, it seems unlikely, as demand for the polymer product, neoprene, has remained fairly constant at around 5-6 Gg/ annum for the past few years, and there is no indication that there will be any significant increase in demand for this product in the near future. It appears that present and future domestic requirements for polychloroprene can be met by imports from the U.S.

# 8.14 MONO- AND DICHLOROBENZENES

## 8.14.1 INTRODUCTION

Chlorobenzene,  ${}^{C}_{6}{}^{H}_{5}{}^{Cl}$ , is a colorless, mobile liquid with a characteristic almond-like odor. It is the first member of the series of chloro-substituted benzenes. Ortho- and meta-dichlorobenzene  $({}^{C}_{6}{}^{H}_{4}{}^{Cl}_{2})$  are both mobile colorless liquids with characteristic aromatic odors. Para-dichlorobenzene is a white crystalline solid with a strong camphor-like odor.

These derivatives are formed when chlorine reacts with benzene at an elevated temperature in the presence of a catalyst. In industrial practice, chlorination of benzene is considered a three-product process. It is not possible to obtain chlorobenzene without some co-production of ortho- and para-dichlorobenzenes. Although by proper choice of catalyst and process conditions, the amounts of dichlorobenzene produced can be minimized.

Chlorinated benzenes were first produced industrially in England in 1909. Chlorobenzene manufacture in the U.S. began in 1915, and became important during World War I when large quantities were required to produce phenol for picric acid manufacture.

Chlorobenzene is presently used in the manufacture of phenol, DDT and dyestuff intermediates. It is also used as a solvent. Orthodichlorobenzene is also used in the manufacture of dye intermediates and as a specialty solvent; it has minor use as an insecticide. Paradichlorobenzene is used principally as a moth control agent, and as a deodorant.

### 8.14.2 PRODUCTION AND USES

Chlorobenzene is produced by direct chlorination of benzene at elevated temperature over a catalyst, usually ferric chloride. Some co-production of dichlorobenzenes occurs, even if the process is optimized for chlorobenzene production. Ortho- and para-dichlorobenzene are the main co-products of chlorobenzene manufacture, and distillation residues from this process are a major source of these chemicals.

Direct production of ortho- and para-dichlorobenzene is by chlorination of chlorobenzene at 150-190 °C over a ferric chloride catalyst. The two principal dichlorobenzenes are separated by distillation or by crystallization of the para-isomer. Meta-dichlorobenzene is usually obtained by isomerization of ortho- and para-dichlorobenzene, by heating at 120 °C under pressure in the presence of aluminium chloride and hydrogen chloride.

There is no manufacture of chlorobenzene or dichlorobenzene in Canada at the present time. The only supplier is Record Chemical Co., Inc. with plants in Quebec and B.C. Record Chemical only produces ortho- and para-dichlorobenzene, probably by purification of imported crude dichlorobenzenes.

Amounts of chlorobenzene used and imported as reported by Statistics Canada are presented in Table 8-5. It can be readily seen from these figures that para-dichlorobenzene is by far the most important of the chlorinated benzenes used in Canada. Its principal uses are in the production of household deodorant formulations, and in the manufacture of moth repellants, having largely displaced naphthalene in the latter

TABLE 8-5 AMOUNTS OF CHLOROBENZENES IMPORTED AND USED

I	N	CANADA

SOURCE	CHEMICAL	1974	1975	1976	REF.
Amounts Imported	Chlorobenzenes	2.51 0g	3.52 Gg	3.85 Gg	3
	monochlorobenzene	n∵a.	n.a.	47.1 Mg	3
	o-dichlorobenzene	n.a.	n.a.	115.8 Mg	3
	p-dichlorobenzene	n.a.	n.a.	3.68 Gg	3
Miscellaneous Chemical Industries (SIC 3799)	p-dichlorobenzene	1.48 Gg	1.24 Gg	n.a.	9
Manufacturers of Soap and Cleaning Compounds (SIC 376)	p-dichlorobenzene	5.00 Mg	n.a.	n.a.	13



n.a. = figures not available

application. Para-dichlorobenzene is also used in the manufacture of dye intermediates and insecticides, but it is believed that there is little or no use of this chemical for these applications in Ontario.

The small amounts of chlorobenzene used in Canada are probably as a speciality solvent or heat exchange medium. The amounts imported are too little to indicate its use in phenol or aniline manufacture.

Ortho-dichlorobenzene is also imported in relatively small amounts.

This suggests that this compound is only used in Canada as a specialty solvent. It is capable of dissolving ferro-oxides, and is thus used in formulations for metal cleaning and polishing, and in formulations to remove lead and carbonaceous deposits from engine parts. With the addition of small quantities of high-boiling alcohols, ortho-dichlorobenzene can be used as a rust-proofing agent. Minor uses could be as a solvent for lacquers and resins, and in insecticide formulations.

## 8.14.3 MARKET FORECAST

Imports of chlorinated benzenes have been rising steadily for the last three years, and it is expected that this trend will continue, particularly for para-dichlorobenzene. However, it is unlikely that production facilities will be built in Canada in the foreseeable future. This is because the current Canadian consumption is only around 4 Gg/annum and a world scale plant for chlorobenzenes production should be capable of manufacturing around 15 Gg/annum. Significant exports would be required for economic operation of such a plant, and as North American demand for chlorobenzene has dropped greatly since 1970 because of the switch to

phenol production via cumene, and the ban on use of DDT (both former major uses of chlorobenzene), there is currently an excess supply of benzene chlorination facilities in North America.

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9 MANUFACTURING PROCESSES AND THEIR
EMISSIONS/DISCHARGES

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## 9.1 INTRODUCTION

Although there are a large number of chlorinated hydrocarbons commercially available, relatively few of these are manufactured in Ontario. Two of the major producers of chlorinated hydrocarbons have facilities in Ontario. Production facilities are located in Sarnia and Cornwall.

Due to the proprietary nature of the manufacturing processes used in the petrochemical industry, information on specific production facilities is not available. Therefore, descriptions of processes and estimates of emissions/discharges are based on information obtained from available literature. Where more than one process is used commercially to manufacture a product, the process that is most likely to be used by the Ontario manufacturer is described.

The processes used in Ontario to manufacture primary chlorinated hydrocarbons are confined to the manufacture of carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane and tetrachloroethylene.

Use of these products as raw materials in the manufacture of secondary products is also discussed, and includes the manufacture of vinyl chloride (produced from 1,2-dichloroethane), tetramethyl lead (produced from methyl chloride) and chlorofluorohydrocarbons (produced from chloroform and carbon tetrachloride).

#### 9.2 CARBON TETRACHLORIDE MANUFACTURE

Processes which are used commercially to manufacture carbon tetrachloride include: chlorination of carbon disulfide and chlorination of methane or propane. In the chlorination of propane, a co-product, tetrachloroethylene, is also produced. This process is reported to be used in Ontario (1) and will be discussed in detail.

#### 9.2.1 FEEDSTOCK

The raw materials required in the chlorination of propane are: chlorine, propane, sulfuric acid, and a catalyst (CuCl<sub>2</sub> and BaCl<sub>2</sub>).

#### 9.2.2 PROCESS DESCRIPTION

The chlorination of propane entails feeding fresh chlorine, recycled chlorine, and propane into a vaporizer where they are mixed with recycled organic chlorides. The recycle diluent rate is normally about 75 percent of the total stream to the vaporizer. The rate is controlled to maintain a reactor temperature of 550 °C to 700 °C. Its composition is also used to control the carbon tetrachloride to perchloroethylene ratio (2).

The reactor effluent, consisting mainly of carbon tetrachloride, perchloroethylene, HCl and excess chlorine is quenched with perchloroethylene. The rapid quench preserves the equilibrium ratio obtained in the reactor and prevents the formation of undesirable by-products.

The quenched stream is charged to a fractionation column which produces a bottom fraction consisting predominantly of perchloroethylene,

and a top fraction containing mostly carbon tetrachloride. The overheads are condensed, with the desired quantity of carbon tetrachloride drawn off as product and the remainder recycled. Non-condensed gases containing organic chloride, hydrogen chloride and chlorine are scrubbed with water to remove the hydrogen chloride, and subsequently dried with concentrated sulfuric acid and purged to remove inert gases formed from impurities present in the raw materials. The remaining chlorine is recycled.

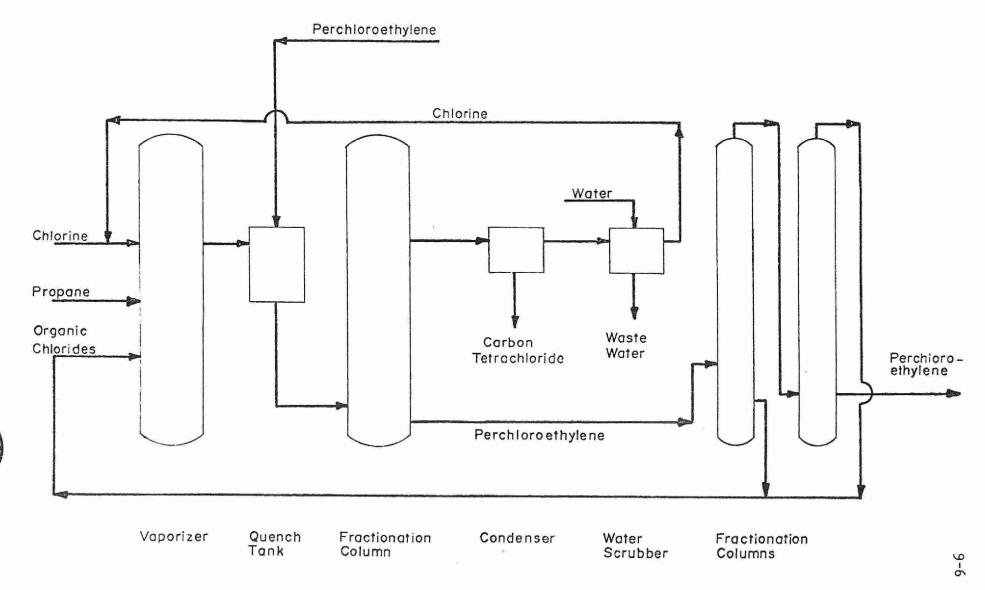
The bottom fraction of the column is fed to a second column, where the heavy ends, consisting mainly of hexachlorobenzene and hexachloroethane, are removed and sent to a recycle surge tank. The overheads from the second column are fed to a third column where the desired quantity of perchloroethylene is removed from the bottom and the top fraction, which is mainly carbon tetrachloride, is sent to recycle.

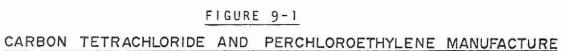
Figure 9-1 is a schematic diagram of a carbon tetrachloride/perchloroethylene manufacturing process.

#### 9.2.3 EMISSIONS/DISCHARGES

The major potential source of air pollution is in the purge on the dry chlorine recycle, which removes inerts. The purge is normally continuous, with chlorine being the pollutant.

No quantitative information on emissions/discharges was found.





## 9.3 DICHLOROETHANE (ETHYLENE DICHLORIDE) MANUFACTURE

1,2-dichloroethane can be manufactured by the reaction of chlorine with ethylene in either the gaseous or liquid phase. Patents have been obtained for processes using this reaction under various specified conditions.

Since 1964, a large portion of the 1,2-dichloroethane manufactured has been switched over the the ethylene oxyhydrochlorination process (3). This process involves the oxyhydrochlorination of ethylene using hydrogen chloride and oxygen.

It is believed that the major Ontario producer uses both the direct chlorination and oxyhydrochlorination processes.

#### 9.3.1 FEEDSTOCK

The input materials to the direct chlorination process are ethylene and chlorine, and for the oxyhydrochlorination process, ethylene, hydrogen chloride, and air.

#### 9.3.2 PROCESS DESCRIPTION

A portion of the ethylene is fed to the direct chlorination process, and a portion to the oxyhydrochlorination process. The reaction of chlorine with ethylene can be conducted in either the liquid or gaseous phase. Catalysts which may be used include ferric, aluminum, copper, and antimony chloride. There are a number of patents which claim the use of various specified conditions for the manufacture of 1,2-dichloroethane. Due to the confidential nature of this process, it was not possible to obtain details of the Ontario operation.

One manufacturing procedure which chlorinates ethylene is described as follows (2):

- Ferric chloride catalyst is suspended in the reactor in ethylene dichloride.
- Ethylene and chlorine react in a fractionation vessel fitted with a reflux condenser.
- 3) The reactor is maintained at 90 °C and 48.2 kPa.
- 4) Gases from the reactor pass through a caustic scrubber where the unreacted gases and trace amounts of hydrogen chloride are removed using a caustic solution.
- 5) The liquid stream from the reactor is sent to a distillation column to remove heavy ends and then to a wash tower, where a caustic wash is used to remove impurities.
- 6) Crude ethylene dichloride is charged to a distillation column for purification. The ethylene dichloride is taken from the top of the tower, with heavy ends removed from the bottom.
- Non-condensed gases from the scrubber are recycled back to the reactor.

In the oxyhydrochlorination process, ethylene, hydrogen chloride (normally recycled from an integrated vinyl chloride manufacturing process), and air are fed to the bottom of the reactor. Although most processes use a fluid catalytic bed, some employ a fixed bed. The reactors are

equipped with internal cooling coils to remove some of the heat produced by the reaction.

The reactor gases are cooled by either a direct quench, or by a heat exchanger, and the ethylene dichloride and water condensed. The ethylene dichloride is separated from the water in a decanter. The uncondensed gases, containing 1 to 5 % ethylene dichloride are further processed in a secondary recovery system using either solvent absorption, or a refrigerated condenser. The off gas from the secondary recovery system is vented to the atmosphere (5).

The crude ethylene dichloride from the decanter is sent to the distillation columns for purification.

Figure 9-2 shows a schematic diagram of a direct chlorination process and an oxyhydrochlorination process, integrated with a vinyl chloride manufacturing facility.

## 9.3.3 EMISSIONS/DISCHARGES

Emissions from the direct chlorination process are relatively small compared to the oxyhydrochlorination process. It is believed that the air pollutants from the direct chlorination process are approximately 1/5 of those emitted from the oxyhydrochlorination process (4).

The only emission source from direct chlorination is the vent on the reflux condenser. An estimate of the emissions from this source are presented in Table 9-1 (6).

Effluent discharges may occur at the gas scrubber and the purification system. Estimates of wastes which may be expected from these sources



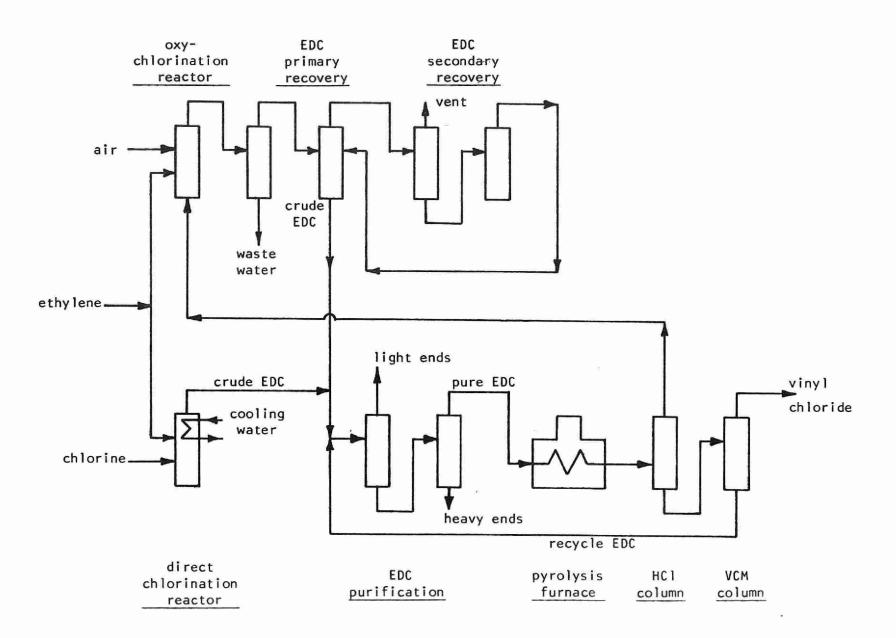


Figure 9-2. ETHYLENE DICHLORIDE AND VINYL CHLORIDE MANUFACTURE

## 1,2-DICHLOROETHANE MANUFACTURE:

## ESTIMATED EMISSIONS FROM THE DIRECT

## CHLORINATION PROCESS

COMPOUND	EMISSION FACTOR (6) kg/MT
Ethane	3.0
Et hy lene	7.5
Methane	3.0
Chlorine	0.0005
Hydrogen Chloride	0.0005

are presented in Table 9-2 (6).

Solid wastes are discharged from the purification section as filter effluent and as bottoms from the distillation column. An estimate of the amount of wastes discharged is presented in Table 9-3 (6).

Gaseous emissions from the oxyhydrochlorination process are from a vent on the ethylene dichloride secondary separator. Estimates of these emissions are presented in Table 9-4 (6).

Discharges from the oxyhydrochlorination process in water effluents are principally hydrogen chloride (0.35 kg/MT of product) (6).

## 1,2-DICHLOROETHANE MANUFACTURE:

## ESTIMATED DISCHARGES FROM THE DIRECT

## CHLORINATION PROCESS

DISCHARGE SOURCE	COMPOUND	EMISSION FACTOR (6) kg/MT
Scrubber	Chlorine	0.9
	Ethylene dichloride	2.5
	Hydrogen chloride	3.8
	Vinyl chloride	0.6
	Methyl chloride	0.05
,	Ethyl chloride	0.05
Purification Section		
Caustic Storage	Ethylene dichloride	0.15
	Sodium hydroxide	0.60
	Sodium Chloride	0.2
Filter Effluent	Ethylene Dichloride	0.3
	Sodium hydroxide	trace



# 1,2-DICHLOROETHANE MANUFACTURE: ESTIMATED SOLID WASTE DISCHARGED FROM THE DIRECT CHLORINATION PROCESS

LOCATION	COMPOUND	EMISSION FACTOR (6) kg/MT
Filter Effluent	Mercuric hydroxide	0.0035
	Tars	trace
	Solids (as carbon)	0.05
Distillation Column	Ethylene dichloride	1.5
	1,1,2-trichloroethane	2.5
	Tetrach loroethane	2.5
	Tars	trace

# 1,2-DICHLOROETHANE MANUFACTURE: ESTIMATED EMISSIONS FROM THE OXYHYDROCHLORINATION PROCESS

COMPOUND	EMISSION kg/MT	
Ethylene	2.70	
Carbon Monoxide	1.20	
Ethylene Dichloride	8.15	
Vinyl Chloride	8.50	
Dichloroethylene	0.45	
Vinylidene Chloride	0.05	
Methane and Ethane (av.)	0.45	

## 9.4 VINYL CHLORIDE MANUFACTURE

Vinyl chloride can be commercially manufactured by either the gas phase reaction between acetylene and hydrogen chloride or by the cracking of ethylene dichloride. As the producer of vinyl chloride in Ontario has a captive source of ethylene dichloride available, the thermal cracking of ethylene dichloride is likely to be the process and is discussed below.

### 9.4.1 FEEDSTOCK

Approximately 2.7 kilograms of ethylene dichloride are required per kilogram of product.

#### 9.4.2 PROCESS DESCRIPTION

Purified ethylene dichloride is cracked in a multi-tubular pyrolysis furnace. A mercuric chloride catalyst is used with the temperature maintained at approximately 450 °C, and the pressure at 410-820 kPa.

The products from the furnace are quenched by direct contact cooling, and separated. HCl gas from the separator is either recovered in a gas absorber or recycled to an oxyhydrochlorination reactor (as shown in Figure 9-1), and the liquid fraction is fractionated to separate the vinyl chloride from the unreacted ethylene dichloride. Vinyl chloride is taken off the top of the column, with the ethylene dichloride taken off the bottom and recycled to the ethylene dichloride purification system. An integrated ethylene dichloride - vinyl chloride process is illustrated schematically in Figure 9-2.

## 9.4.3 EMISSIONS/DISCHARGES

The major source of gaseous emissions is from the tail gas absorber.

An estimate of the emissions from this source is presented in Table 9-5

(6).

kg/MT product

Solid waste is produced at the filter in the ethylene dichloride purification step. Estimated quantities are as follows (7):

Ethylene dichloride	0.8
Tars (as C <sub>2</sub> HCl)	0.05
Solids (as carbon)	0.2

# ESTIMATED EMISSIONS FROM

## VINYL CHLORIDE MANUFACTURE

	VINYL CHLORIDE kg/MT
Hydrogen chloride	0.1
Vinyl chloride	5.0
1,2-dichloroethylene	0.15
l,l-dichloroethylene	0.4
Acetylene	1.5

## 9.5 TRICHLOROETHANE MANUFACTURE

Although both 1,1,2-trichloroethane and 1,1,1-trichloroethane are commercially available, only 1,1,1-trichloroethane is produced in Ontario.

#### 9.5.1 FEEDSTOCK

Vinyl chloride, hydrogen chloride, and chlorine are the input materials required in the manufacture of l,l,l-trichloroethane.

#### 9.5.2 PROCESS DESCRIPTION

1,1,1-trichloroethane is made in two steps. First, vinyl chloride
is hydrochlorinated in the liquid phase to produce 1,1-dichloroethane.
In the second step, 1,1-dichloroethane is thermally chlorinated to produce
1,1,1-trichloroethane and hydrogen chloride.

1,1-dichloroethane vapor is fed along with chlorine gas to a tower type reactor at 400 °C, and atmospheric pressure. The reaction produces 1,1,1-trichloroethane and hydrogen chloride at a yield of approximately 95 %. The 1,1,1-trichloroethane and HCl from the reactor are cooled at about 40 °C, mixed with fresh vinyl chloride, and fed to a tower type hydrochlorinator in which a liquid mixture of 1,1-dichloroethane and 1,1,1-trichloroethane containing ferric chloride catalyst is recirculated. The hydrogen chloride reacts with vinyl chloride to produce 1,1-dichloroethane.

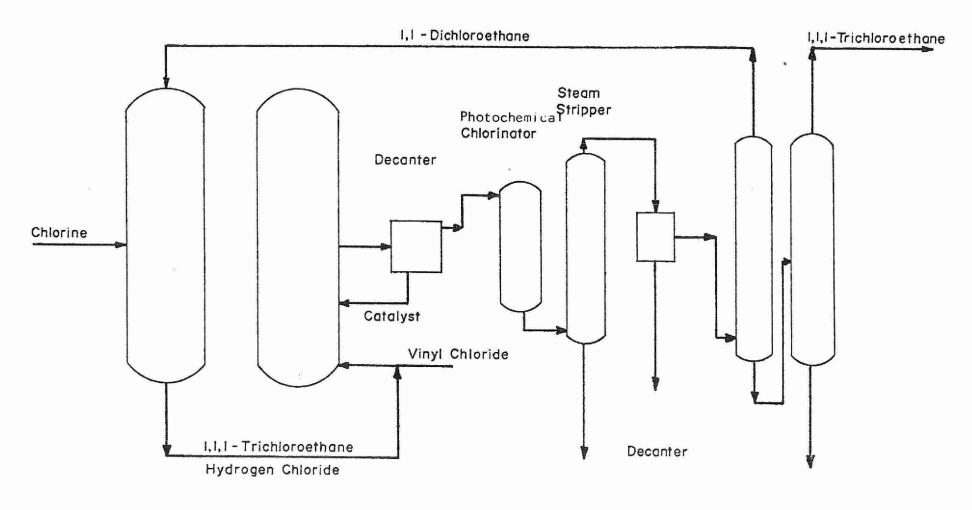
The products from the hydrochlorinator are decanted from the catalyst and fed to the purification-separation system.

In the purification system, the chloride contents of the products from the hydrochlorinator are adjusted by a photochemical chlorination.

The products are stripped from the heavy materials by steam distillation, decanted from the condensed steam, and dried. From the drier the products are fed to the first distillation column, where the 1,1-dichloroethane is stripped off and recycled. The bottom fraction from the first distillation column is fed to the second distillation column, where the 1,1,1-trichloroethane is taken off overhead. The manufacturing process for 1,1,1-trichloroethane is illustrated schematically in Figure 9-3.

## 9.5.3 EMISSIONS/DISCHARGES

There are two major sources of potential air pollution; the vent on the hydrochlorinator, to prevent inert gases from building up, and from a purge on the recycled 1,1-dichloroethane line. Emission rates from these sources are not known.



Distillation Columns

Chlorinator

Hydrochlorinator

Purification System

7-6

## 9.6 TETRACHLOROETHYLENE MANUFACTURE

Processes which can be used to produce tetrachloroethylene (perchloroethylene) commercially include:

- chlorinating trichloroethylene to pentachloroethane and dehydrochlorinating pentachloroethane to tetrachloroethylene
- chlorination of 1,1,2,2-tetrachloroethane
- chlorination of acetylene
- chlorination of propane

Of these processes, the chlorination of propane is by far the most popular, and is the one used in Ontario.

#### 9.6.1 FEEDSTOCK

## 9.6.2 PROCESS DESCRIPTION

Chlorination of propane involves the feeding of fresh chlorine, recycled chlorine, and propane into a vaporizer where they are mixed with recycled organic chlorides. The recycle diluent rate is normally about 75 percent of the total stream to the vaporizer. The rate is controlled to maintain a reactor temperature at 550 °C to 700 °C. Its composition is also used to control the carbon tetrachloride to perchloroethylene ratio.

The reactor effluent consisting mainly of carbon tetrachloride, perchloroethylene, HCl and excess chlorine is quenched with a liquid,

normally perchloroethylene. The rapid quench preserves the equilibrium ratio obtained in the reactor and prevents the formation of undesirable by-products.

The quenched stream is charged to a fractionation column which produces a bottom fraction which is predominantly perchloroethylene, and a top fraction containing mostly carbon tetrachloride. The overheads are condensed, with the desired quantity of carbon tetrachloride drawn off as product and the remainder recycled. Non-condensed gases containing organic chlorides, hydrogen chloride and chlorine are scrubbed with water to remove the hydrogen chloride, and subsequently dried with concentrated sulfuric acid and purged to remove inert gases formed from impurities in the raw materials. The remaining chlorine is recycled.

The bottom fraction of the column is fed to a second column, where the heavy ends consisting mainly of hexachlorobenzene and hexachloroethane, are removed and sent to a recycle surge tank. The overheads from the second column are fed to a third column where the desired quantity of perchloroethylene is removed from the bottom and the top fraction, mainly carbon tetrachloride, is recycled.

## 9.6.3 EMISSIONS/DISCHARGES

The major potential source of air pollution is in the purge on the dry chlorine recycle, which removes inert gases. The purge is normally continuous with chlorine being the pollutant (7).

No quantitative information on emissions/discharges was found.

## 9.7 TETRAMETHYL LEAD MANUFACTURE

The two major processes used in the production of tetramethyl lead are the batch alloy process and the electrolytic Grignard process. It is believed that the Ontario producers of tetramethyl lead use the batch alloy process.

#### 9.7.1 FEEDSTOCK

The input materials required in the batch alloy process are: methyl chloride, sodium-lead alloy, and a catalyst. Typical catalysts are Lewis acids of the aluminium halide type and alkyaluminium compounds.

#### 9.7.2 PROCESS DESCRIPTION

The principal reaction in the process is:

$$4NaPb + 4CH_3C1 \rightarrow (CH_3)_4Pb + 4NaC1 + 3Pb$$

The first step in the process is to make the sodium-lead alloy by combining molten metallic lead with metallic sodium in a melt pot in the ratio of 40 to 10 by weight. The alloy, NaPb, is then loaded into hoppers, in sufficient quantity for one charge. The contents of the hoppers are dumped into horizontal autoclaves (8).

The methyl chloride is fed to the autoclave from weigh tanks over a period of several hours. A further 30-60 minute cook period is required after the methyl chloride feeding has stopped. Vaporized alkyl halides are vented from the autoclave into a reflux condenser, and returned to the autoclave. Upon completion of the reaction the autoclave is vented and the products discharged into a steam still.

In the still, the tetramethyl lead is separated from the by-product lead and sodium chloride by direct steam stripping. The tetramethyl lead and steam are condensed and sent to a decanter. In the decanter, the water rises to the top, and the tetramethyl lead is taken off as a bottom stream. The upper aqueous layer in the decanter, containing unreacted methyl chloride and dissolved organic by-products is sent to a waste water treatment facility.

The sludge bottoms from the still are sent to a lead recovery unit and the concentrate is combined with the supernatant from the tetramethyl lead decanter and discharged into a settling basin for final lead recovery. A tetramethyl lead manufacturing process is illustrated schematically in Figure 9-4.

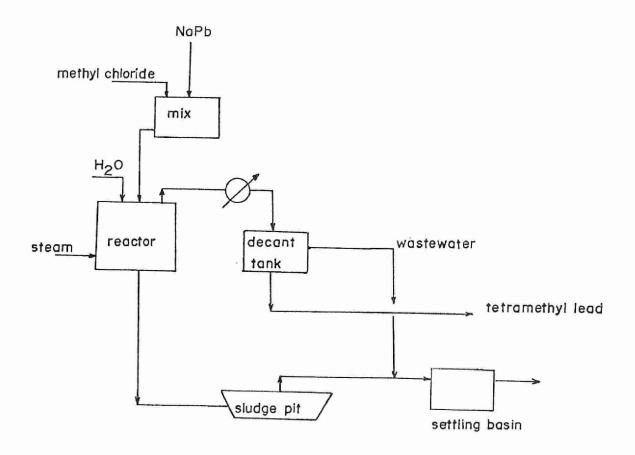
## 9.7.3 EMISSIONS/DISCHARGES

Potential points of emission are from the venting of the autoclave, and venting of an inert gas which is used to blanket the reaction mass during the transfer of the reaction mass from the autoclave to the still.

The major potential for water pollution is the aqueous portion from the decanter. One water analysis conducted on a waste stream from a tetraethyllead plant is given below (2).

Flow	100 litres per kilogram
COD	1,100 millograms per litre
BOD <sub>5</sub>	40 millograms per litre
TOC	56 millograms per litre

As the tetraethyl and tetramethyllead processes are similar, a similar waste stream may be expected from a tetramethyl lead process.



MANUFACTURE OF TETRAMETHYL LEAD FROM METHYL CHLORIDE



## 9.8 CHLOROFLUOROHYDROCARBON MANUFACTURE

A large portion of the chloroform and the carbon tetrachloride in Ontario is used in the manufacture of chlorofluorohydrocarbons. The most common method of manufacture is the successive replacement of chlorine by fluorine, using hydrogen fluoride.

## 9.8.1 FEEDSTOCK

The input materials for chlorofluorohydrocarbon manufacture are: chlorinated hydrocarbons such as chloroform or carbon tetrachloride, hydrofluoric acid and a catalyst such as fluorinated antimony pentachloride.

## 9.8.2 PROCESS DESCRIPTION

The chlorinated hydrocarbon is fed into a reactor and mixed with hydrofluoric acid. The temperature, pressure and fluoride concentration are regulated to control the degree of fluorination. The reaction can be either batch or continuous.

The reaction products are purified by distillation and by scrubbing through water and slightly alkaline solution. The products are dried by passing them, in the liquid phase, through beds of silica gel, alumina gel or synthetic zeolites (9).

## 9.8.3 EMISSIONS/DISCHARGES

The major source of emission is from a vent on the distillation column. When lighter fractions of the chlorofluorohydrocarbons are inadvertently produced, they are vented to the atmosphere. However, no data are available on the quantity of these emissions. Fugitive emissions of the chlorinated hydrocarbon raw material are negligible.

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10 <u>EMISSION AND DISCHARGE</u>

<u>CONTROL TECHNOLOGY</u>

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#### 10.1 SUMMARY

#### Air Emission Control

Air emission control systems are usually an integral part of manufacturing technology. As a consequence, process data are considered proprietary, and are usually not published. Thus very little information can be found in literature.

Condensation, absorption, adsorption and incineration are the most frequently used systems in controlling emissions from stationary sources.

If a multistage condensation system with refrigeration in the final stage is used, an overall removal efficiency of 99+ % can be achieved for most of the hydrocarbons of interest here.

Water, mineral oils, non-volatile hydrocarbon oils and various aqueous solutions are used for the absorption of hydrocarbons, which are usually contained in large volume gaseous streams. Absorption systems can be designed to achieve up to 90 to 95 % removal efficiency.

Adsorption on the surface of specially prepared granular solids, and adsorbents, is a very efficient method for the selective removal of hydrocarbons from gaseous streams. Activated carbon is the most widely used adsorbent. Practical sorption capacities for activated carbon vary from 6 weight % for benzene to 20 weight % for perchloroethylene.

Recently, Dow Chemical has developed a new copolymer adsorbent



which is suitable for the control of emissions of benzene, styrene, toluene, methylene chloride, allyl chloride and a number of other compounds. Insufficient experimental data exist to design an adsorption system of optimum efficiency. The development of new high capacity sorbents should be encouraged.

Incineration is a frequently used method of emission control in the petrochemical industry. 1000 °C and 2 seconds of retention time is considered satisfactory for the destruction of most organic compounds, if adequate mixing is assured by proper design. An inadequate supply of waste gases creates problems in operating an incinerator and if the off-gases are not corrosive, some form of heat recovery is desirable. An overall thermal efficiency of 60 to 80 % may be achieved.

A catalytic oxidation system reduces heat requirements by lowering the oxidation temperature. Deactivation of the catalyst and often an inadequate incineration efficiency are the main problems associated with catalytic oxidation.

Flares are not considered as environmentally satisfactory for the disposal of hazardous gases, because of incomplete combustion and noise pollution problems.

In a modern petrochemical plant, hydrocarbons are stored in a totally enclosed storage vessel. Up to 85 % reduction of emissions may be achieved by installation of a floating roof in preference to a fixed roof vessel. However, recovery units based on the adsorption principle may quantitatively eliminate emissions from fixed roof tanks.

It is estimated that 60 to 80 % of all storage facilities in Canada utilize floating roofs or their equivalents to reduce hydrocarbon losses.

Fugitive sources are one of the largest categories of hydrocarbon emissions. They include: pump seals, relief valves, pipeline valves, sampling and blind changing. There are two major studies underway in the U.S.A. to determine fugitive hydrocarbon emissions.

#### Waste Water Effluent Control

Large amounts of nonsolubilized aromatic hydrocarbons and other oils can be removed by:

- gravity oil-water separation to produce an effluent containing down to 50 ppm oil
- induced air flotation (IAF), dissolved air flotation
   (DAF) or filtration to produce an effluent containing
   10-20 ppm oil
- biological oxidation or activated carbon adsorption to produce an effluent containing <10 ppm.</li>

Soluble aromatic hydrocarbons may be removed from waste water effluents by biological oxidation. However, for many aromatics the process is slow and other methods may have to be applied.

Activated carbon is normally used as a final polishing step for complete contaminant removal. Nonpolar hydrocarbons of molecular weight greater than 45 are adsorbable on carbon. The feasibility of activated carbon adsorption should be determined by both carbon



adsorption isotherms and continuous flow pilot plant simulation tests. Polymeric adsorbents are being developed and offer better sorption properties for specific compounds.

A complete removal of hydrocarbons from waste water effluents can be achieved by:

- primary treatment such as gravity oil-water separation and IAF, DAF or filtration followed by
- the series: biological oxidation carbon adsorption treatment or
- the series: carbon adsorption biological oxidation treatment or
- carbon adsorption as the only treatment

Other available technologies are steam stripping, solvent extraction, membrane processes and wet air oxidation.

### Waste Disposal Methods

Incineration is an ultimate disposal method if properly designed and operated. 1000 °C and 2 seconds residence time is considered adequate for the thermal destruction of most organic compounds. Incomplete combustion of chlorinated hydrocarbons may result in emissions of phosgene and chlorine. Excess hydrogen is required to form hydrogen chloride, which may be neutralized or recovered in the form of 15-20 % acid. When extractive distillation is used, higher grade acid may be produced.

No more than 10 ppm of chlorine and hydrogen chloride have been reported in the hydrogen chloride recovery plant tail gas.

Cement kiln incineration is a safe disposal method for organic compounds, particularly for chlorinated materials, where the formation of chloride ion has been found to improve the quality of the cement produced.

Deep wells and land fills have often been used in the past to dispose of chemical wastes. However, it has become more and more difficult to find sites for disposal where there is no risk of ground water contamination.

With the latest processing technology, the production of waste in petrochemical plants is significantly minimized.

#### 10.2 AIR EMISSION CONTROL

Little information is available on the usage of air pollution control systems in hydrocarbon-producing and -consuming industries. The aromatic hydrocarbons of interest here are usually produced by integrated petrochemical plants, where they are also used as intermediates, as discussed in Section 8. Processes producing and/or using aromatic hydrocarbons have recovery systems as an integrated part of their technology.

The most frequently used systems are condensation, absorption, adsorption and incineration.

#### 10.2.1 STATIONARY SOURCES

#### 10.2.1.1 CONDENSATION

Condensers have found a wide range of applications in the organic chemical industry, where their purpose has been to condense concentrated vapors in the primary process. Control of organic emissions by condensation is limited by the equilibrium partial pressure of the component. As condensation occurs, the partial pressure of the compound remaining in the gas phase decreases rapidly and complete condensation is not possible. For example, even at 0 °C, toluene has a vapor pressure of about 0.8 kPa; at atmospheric pressure (101.3 kPa), a gas stream saturated with toluene still contains about 8,000 ppm of that gas. For this reason, condensers are usually followed by a secondary system such as an adsorber, absorber or incinerator.

Condensation is mostly utilized to remove a relatively high hydro-

carbon concentration from small noncondensable waste gas flows. The main advantage of condensation is that the product may be recovered at relatively low energy requirements and cost (1). Hydrocarbon removal efficiency depends on:

- composition of the waste stream
- operating temperature
- condenser design

and may vary between 40 and 99.9 %.

Since condensation is usually accomplished by decreasing the temperature of the vapor, a cold surface or a cooling liquid is depłoyed in the gas stream to induce condensation. Condensers may be classified into two groups: surface and contact.

Surface Condensers include the common shell-and-tube type heat exchanger in which the cooling medium, usually water, flows through the tubes, and vapor condenses on the outside surface. The condensed vapor forms a film on the cool tubes and drains to storage for further recovery of valuable compounds or incineration. Cooled condensers are usually designed with finned tubes, and the vapor condenses outside the tubes.

A series of two, three or more heat exchangers (condensers) may be used to improve the removal efficiency. Different cooling media may also be used in individual stages as shown in Figure 10-1. A very low temperature in the third stage with refrigeration is needed for an overall removal efficiency of 99+ % (2,13). This may cause operational problems if water vapor is present (Figure 10-1).

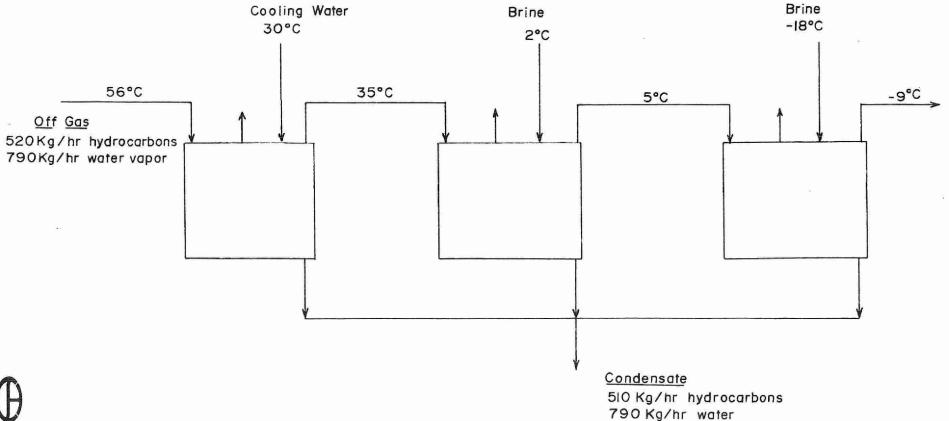


FIGURE 10-1

Surface condensers are used, for example, in styrene production processes to control benzene emissions from distillation columns. It is reported (6) that the benzene emissions were reduced to  $4.0 \times 10^{-3} \text{ kg/kg}$  styrene produced.

Contact Condensers cool the vapor by spraying a cold liquid directly into the gas stream. The condensed vapor and cooling liquid mixture is then treated in a recovery unit or effluent control plant. Contact condensers are, in general, less expensive, more flexible, and more efficient in removing organic compounds, than surface condensers. However, the cost of recovering hydrocarbons from the cooling medium may not improve the overall economics of a contact condensation system.

J.R. Fair (12) outlines the design procedures for an optional contact condenser system.

Both contact and surface condensers can be easily applied to elevated pressure technology. Elevated pressure proportionately increases the vapor pressure of condensable hydrocarbons. This results in better removal efficiency (6, 44). For example: a condenser treating the oxidizer vent from a cumene manufacturing process operates at 506 kPa and reduces the benzene emissions to  $10^{-5}$  kg/kg of cumene produced. Condensers have been used successfully, either separately or with additional controls, in a number of processes such as (14, 19): alkylation unit accumulator vents, styrene processing units, toluene recovery accumulation vents, UDEX extraction units and solvent recovery systems.

Unfortunately, no detailed operating data are available in the literature as these data are considered to be an integral part of

proprietary technology.

Fog formation is a potentially serious yield loss and pollution problem for all processes that involve partial condensation. D.E. Steinmeyer (15) presents a number of examples of fog formation in the cooling systems of streams containing benzene, carbon tetrachloride, trichloromethane and chlorobenzene. In order to minimize fog formation it is suggested (15):

- to use lower temperature differences in the condenser
- to obtain uniform cooling

#### 10.2.1.2 ABSORPTION

Absorption of hydrocarbons in the petrochemical industry is an important manufacturing step. As with condensation, absorption is considered a preliminary step in air pollution control because it does not remove enough of the hydrocarbons to provide a complete control. This technique is used commonly, and is often found to be profitable in petroleum and petrochemical operations for gaseous streams with a relatively high concentration of hydrocarbons.

Common absorbents for organic vapors are water, mineral oil, non-volatile hydrocarbon oils and various aqueous solutions (2-5)

In the absorption process, a soluble component of a gas mixture is dissolved in a relatively non-volatile liquid. Condensation operations may precede this absorption process (1, 6, 7). The ideal absorbent should meet most of the following requirements (8):

- the gas (to be absorbed) should be quite soluble in the

absorbent to enhance the rate of absorption and to decrease the quantity of absorbent required

- the absorbent should be relatively non-volatile to prevent losses and contamination of the gaseous stream
- the absorbent should be non-corrosive to reduce maintenance costs
- the absorbent should have a low viscosity to increase absorption and reduce flooding (packed towers)
- the absorbent should be low in toxicity, non-flammable,
   chemically stable and have a low freezing point

Creosote oil or gas oil is commonly used for the absorption of benzene, toluene and xylenes (9). A common practice is the use of tower scrubbers in which the gas and wash oil flow counter-currently. The factors which influence the absorption system performance are:

- temperature
- gas/oil ratio
- quality of oil

Operating temperatures should be as low as practicable in order to reduce hydrocarbon vapor pressure in the oil. The gas/oil ratio may vary from 1 to 5 m<sup>3</sup> of oil per 100 m<sup>3</sup> of gas depending on the type of tower, the concentration of hydrocarbons in the inlet stream, the outlet concentration, and the physicochemical properties of the wash oil. The "drop point" of the wash oil should be about 200 °C and the boiling point between 200 and 300 °C. Creosote oil has a higher sorption capacity than gas oil (4 % vs 3 % by weight). Viscosity is the most

important property of wash oils for use in this application and should be between 30 and 35 sec Redwood at 20  $^{\circ}\text{C}$ .

It is reported that an absorption system is capable of reducing the emissions of a benzene-toluene mixture from a styrene recovery plant to 3 to  $4 \times 10^{-3}$  kg/kg of styrene and about  $3 \times 10^{-3}$  kg of ethylbenzene/kg of styrene. A 90 to 95 % absorption efficiency of benzene has been reported (10).

A detailed description of absorption towers and design procedures has been published (8, 9).

#### 10.2.1.3 ADSORPTION

Adsorption processes for gas purification are based on the physical properties of specially prepared granular solids, known as adsorbents, which selectively attract and retain gases on their surfaces (11, 16, 21, 22). The most widely used adsorbents are activated alumina, activated carbon, silica gel and molecular sieves. An adsorption process operates on a cyclical basis. The gas and adsorbent are contacted until the desired point of saturation is reached; the adsorbent is then removed from the gas stream and desorbed.

All adsorption processes are exothermic. The heat of adsorption due to surface attraction is greater than the heat of condensation of the gases being adsorbed.

Adsorption increases progressively with increase in the partial pressure of the gas. At low partial pressure, adsorption is by surface attraction, and at higher partial pressures the smallest wetted

capillaries become effective and condensation begins. At higher pressures the larger capillaries become effective (Figure 10-2 shows the relationship between maximum effective pore size and vapor pressure (or vapor concentration) for benzene at 20 °C as computed on the basis of the capillary condensation theory (9)). The relationship between pressure and amount adsorbed depends upon:

- the pore size distribution of the adsorbent
- the exposed surface area
- the nature of the sorbent and gas

This relationship is expressed graphically in the form of adsorption isotherms and must be determined experimentally. The adsorption isotherms are expressions of the amount of gas adsorbed under true static equilibrium conditions (Figure 10-3, 10-4).

Very little quantitative data are available on the adsorption of a mixture of gases and vapors. A preferentially adsorbed gas will displace other gases which have already been adsorbed.

The application of adsorption in air pollution control involves the use of a dynamic system (20, 21). The adsorbent is generally used in a fixed bed and the contaminated air or gas is passed through it.

Depending on the amount collected and its market value, the contaminant is either recovered or discarded when saturation of the adsorbent necessitates regeneration. Although isotherms (for static conditions) are indicative of the efficiency of an adsorbent, they do not supply data to enable the calculation of contact time or the amount of adsorbent required to reduce the contaminant concentration below the

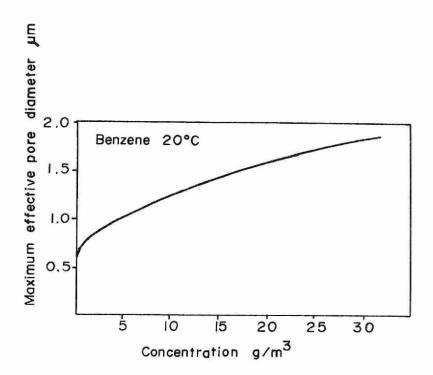
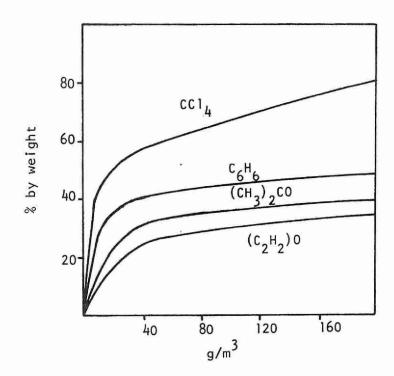


FIGURE 10-2

RELATIONSHIP BETWEEN PORE SIZE AND VAPOR CONCENTRATION





 $\frac{\text{FIGURE 10-3}}{\text{.}}.$  ADSORPTION ISOTHERMS FOR SOLVENTS ON ACTIVATED CARBON

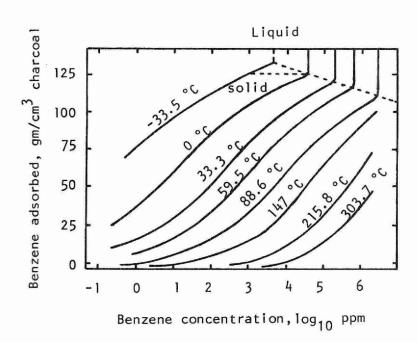


FIGURE 10-4

ADSORPTION ISOTHERMS OF BENZENE ON ACTIVATED COCONUT CHARCOAL

AT ATMOSPHERIC PRESSURE (3)



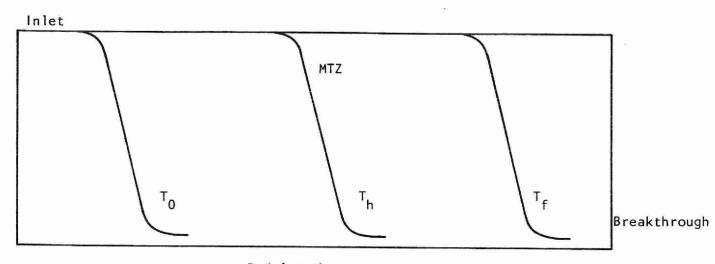
desired limits.

When a gas is first passed through a bed of adsorbent, most of the contaminants are initially adsorbed at the inlet part of the bed.

Later, when the adsorbent at the inlet end becomes saturated, adsorption takes place further along the bed.

The situation in the bed while it is in normal operation may be represented by Figure 10-5. That portion of the bed in which the adsorbate concentration transition occurs is defined as the masstransfer-zone (MTZ) (16). As more gas is passed through, the saturated zone moves forward until the breakthrough point is reached, at which time the exit concentration begins to rise rapidly above whatever limit has been fixed as a desirable maximum. While the concentration at saturation is a function of the adsorbent material used and the operating temperature, the dynamic capacity is also dependent on other operating conditions such as inlet concentration, gas flow and bed depth. It is extremely important that the adsorber bed should be at least as long as the transfer zone length of the key compound to be adsorbed. Therefore, it is important to know the depth of this mass transfer zone. The following factors play the most important role in dynamic adsorption and the length and shape of the MTZ:

- i) the type of adsorbent
- ii) the particle size of an adsorbent
- iii) the depth of the adsorbent bed
- iv) the gas velocity
- the temperature of the gas stream and the adsorbent



Bed length

 $T_0$  = MTZ concentration gradient at the formation of the zone

 $T_{h}$  = MTZ concentration gradient at half life

 $T_f = MTZ$  concentration gradient at breakthrough



# FIGURE 10-5

- vi) the concentrations of the contaminants to be removed
- vii) the concentrations of the compounds not to be removed, including moisture
- viii) the pressure of the system
- ix) removal efficiency
- x) possible decomposition or polymerization of contaminants on the adsorbent

## i) Selection of Adsorbent

The preferential adsorption characteristics and physical properties of the industrial adsorbents determine their main applications. All of the adsorbents are capable of adsorbing organic solvents, impurities and water vapor from the gas stream, but each has a particular affinity for water vapor or organic vapors. Activated carbon is the most commonly used for organic vapors. The main advantage is its ability to recover organic solvents present at low concentrations in the gas stream. For satisfactory adsorption, the molecular weight of a substance should be greater than 45; benzene and the other hydrocarbons of interest here easily meet this requirement. The following is a partial list of compounds selectively adsorbed by activated carbon (2): benzene, carbon tetrachloride, chloroform, cumene, dichloroethane, dichloroethylene, perchloroethylene, toluene and trichloroethylene. R.R. Manzone and D.W. Oaks (17, 18) report some practical sorption capacities (% by weight for activated carbon):

Benzene

6 %

Carbon Tetrachloride

10 %

Chloroform	10 %
Perchloroethylene	20 %
Toluene	7 %
Trichloroethylene	15 %
Xylene	10 %

Yun-Chung Sun and F.R. Killat of Dow Chemical (39) have described a new co-polymer adsorbent for the control of emissions of benzene, styrene, toluene, methyl ethyl ketone, methylene chloride, allyl chloride, pentane, hexane, gasoline, etc.

### ii) The Effect of Particle Size

The dimensions and shape of the adsorbent particles affect both pressure drop through the adsorber bed and the diffusion ratio into the particles. Adsorber beds consisting of smaller particles, although causing a higher pressure drop, are more efficient and will produce a smaller MTZ.

### iii) The Depth of the Adsorber Bed

It is primarily important that the depth of the bed be larger than the unsaturated length of the transfer zone. Secondly, a more than proportional increase of capacity is achieved for any multiple of the minimum bed depth. The MTZ is usually determined by experiment.

#### iv) Gas Velocity

The velocity of the gas stream through the adsorbent bed is limited by the adsorbent crushing velocity. The length of the MTZ is directly proportional to velocity. In practice, however, volume velocity is usually used and for most common activated carbons, a volume velocity of 1 1/sec can be treated by 50 kg of carbon (17, 18). Properly conducted pilot plant tests can significantly optimize the operating parameters.

#### v) Temperature

Generally, adsorption decreases with increasing temperature. The equilibrium capacity of adsorbents is lower at higher temperatures; the dynamic capacity is also lower. Figure 10-6 shows the variation of benzene vapor adsorption on carbon with temperature. Most carbon adsorbents are satisfactory for use up to 150 °C.

## vi) Concentration of Contaminant

The adsorption capacity of adsorbents is directly proportional to the concentration of the contaminant. It is also inversely proportional to the length of the MTZ; for example, a deeper bed will be required to remove a lower concentration contaminant with equal efficiency than to remove the same contaminant at higher concentrations. It is very important that, for combustible gases, the concentration entering the adsorbent is kept below the lower explosive limits (17, 18):

Benzene 1.4 % (volume in air)

Toluene 1.27 %

Ortho-xylene 1.0 %

Para-xylene 1.1 %

Concentrations on the order of 25-50 % of the lower explosive limit are used in commercial practice (9).

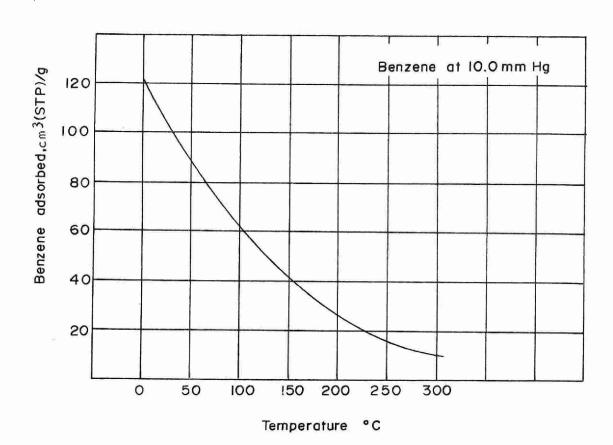


FIGURE 10-6

# BENZENE ADSORPTION ISOBAR ON CARBON



In general, fixed bed adsorbers have not been used to recover organic vapors when the vapor-laden stream contains less than 2,700 ppm (2). There is a range of vapor concentration for which profitable recovery of organics cannot be obtained. This range, between a few ppm and about 1000 ppm, is often unsuitable for non-regenerative systems because of the high cost of adsorbent replacement. For such a range, instead of desorption, oxidative regeneration of the adsorbent has been suggested (2).

## vii) Concentration of the Compounds not to be Removed

It is important to realize that some portion of all gases present will be adsorbed because these gases compete for the available surface area. Although activated carbon is less sensitive to moisture than other adsorbents, its adsorption capacity in the presence of water vapor can be considerably lower than adsorption from a dry gas stream. It is preferable to adsorb organics from a low relative humidity gas stream.

#### viii) Effect of Pressure

Generally, the adsorption capacity of the adsorbent increases with increasing pressure. However, at high pressures (over 3.5 MPa) a decrease in capacity is observed due to retrograde condensation and increased adsorption of the carrier gas.

#### ix) Removal Efficiency

Removal efficiency is an important design parameter and depends on the needs of the plant. Naturally, deeper adsorbent beds are required to achieve a 99.9+ % single pass removal, than for a partial 60-80 % removal efficiency.

## x) Decomposition and Polymerization

Some hydrocarbons may decompose, react or polymerize when in contact with the adsorbent. The decomposed product may be adsorbed at a lower capacity than the original substance. Polymerization on the adsorbent surface will significantly lower its adsorption capacity.

### Adsorption Systems

Adsorption systems may be classified as

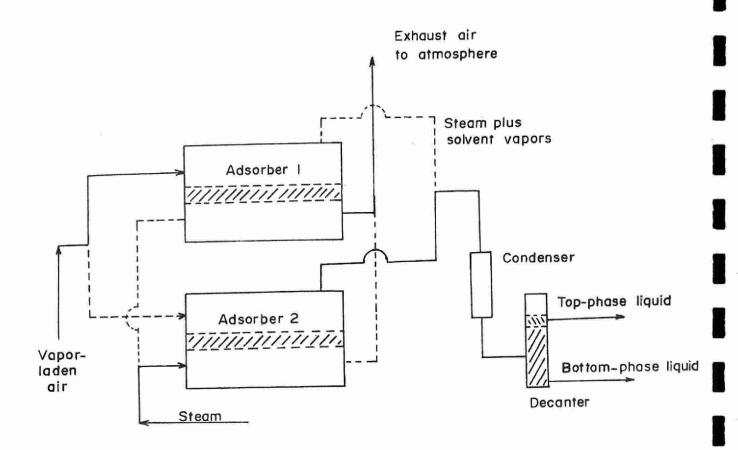
- regenerative or
- non-regenerative

Regenerative systems are used when the adsorbent is to be reactivated by desorption and the desorbed vapors recovered for reuse or disposal (Figure 10-7).

Non-Regenerative systems are used when the adsorbent is to be replaced with fresh materials; the displaced material is sent for central regeneration or for disposal. It is usually used for small commercial applications, and will not be discussed in this report.

#### Regenerative Adsorption Systems

A desirable feature of using an adsorption system for the control of hydrocarbon emissions is its ability to recover the adsorbed hydrocarbon on regeneration. To remove the adsorbate, the sorbent must be heated to a temperature above that at which the hydrocarbon was adsorbed. Desorbed vapors are removed by a carrier gas, usually steam.



## FIGURE 10-7

## TWO-UNIT FIXED-BED ADSORBER (2)

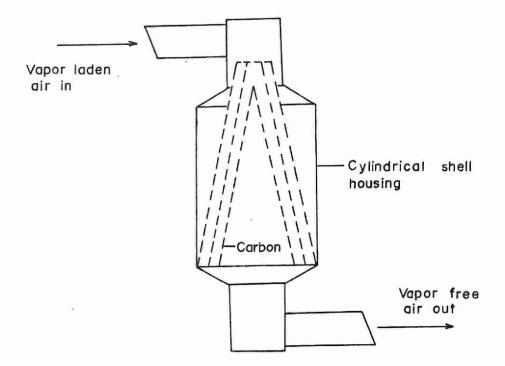


The steam passes through the bed at 1/10 or 1/5 of the air velocity, heats the bed, and carries desorbed hydrocarbons from the adsorber to a condenser (Figure 10-7) where hydrocarbons and steam are condensed. The hydrocarbons are then separated from the condensed water. Hot air and a partial condenser may also be used. A well-designed plant will have a steam consumption in the range of 1 to 10 kg of steam per kg of recovered hydrocarbon (9, 19). Steam consumption for desorption of toluene and perchloroethylene is discussed in detail by J.A. Danielson (19). R.D. Fulker (11) outlines all of the factors which must be considered in designing the desorption process.

The adsorption process involves mass transfer as well as adsorption, and no adequate design and scale up procedures are available which include this consideration (2). In actual practice, the adsorption capacity, height of the bed, and stripping conditions for a given gas stream and type of hydrocarbon are obtained experimentally in pilot plant units (Figure 10-8) and the design data are considered proprietary (20).

Activated carbon sorbent beds are identified as effective emission control devices for recovering cumene. Pressure and temperature conditions for the stream entering the carbon bed are such that a relatively high cumene content is present and a recovery efficiency of between 82 and 91 % is achieved (36). W.D. Lovett and F.T. Canniff (45) report the application of carbon adsorption in combination with incineration, with fuel economy as the main objective. Air containing 85 ppm of benzene is concentrated to 3,500 ppm and incinerated. The effect of concentration is an 86:1 reduction of energy requirements.





# FIGURE 10-8

VERTICAL ADSORBER WITH TWO CONES (permitting studies on different depths of carbon beds)(2)



## 10.2.1.4 INCINERATION

Incineration is another process for the control of gaseous, liquid or solid wastes. The objective is to oxidize as completely as possible organic materials emitted and/or discharged from a process or operation. It is essentially a straightforward combustion process in which oxygen (in air) must be mixed with the combustible at some temperature above its autoignition temperature. Typical values of autoignition temperatures for some hydrocarbons are listed below (23, 24).

	°C
Toluene	508
Styrene	490
Ethane	515
Ethylene	450
Benzene	498
Ethy lbenzene	432
o-Xylene	464
m-Xylene	528
p-Xylene	529
Styrene	490
Naphthalene	526
Methyl Chloride	632
Ethyl Chloride	519
Dichloroethylene	460
Trichloroethane	486
Trichloroethylene	420

When starting with a waste in liquid form, it is necessary to supply sufficient heat for evaporation in addition to raising it to its ignition temperature.

There are a number of different types of incinerators used to oxidize gaseous materials and they can be classified into 3 categories:

- i) flares
- ii) direct flame
- iii) catalytic oxidation

### Flares (29)

Large volumes of hydrocarbon gases are produced and handled in a modern petrochemical plant. Usually these gases are controlled within the process. Sudden or unexpected upsets and scheduled shut-downs in the process units, however, can produce gas in excess of the capacity of the hydrocarbon recovery system.

Emergencies that can cause the sudden venting of excessive amounts of gases and vapors include fires, compressor failures, over-pressures in process vessels, line breaks, leaks and power failures.

Excess gas is usually incinerated in flares. Flares are mostly elevated to safely dissipate heat and disperse any vapors that may be emitted. Smoke is a by-product of incomplete combustion. Smokeless combustion can be obtained in an elevated flare by the injection of an inert gas to the combustion zone to provide turbulence and inspirate air. The most commonly used air-inspirating material is steam. However, smokeless burning of large quantities of gases by flares presents some

serious design problems. Flares are generally not environmentally satisfactory for disposal of hazardous gases because of incomplete combustion, breakdown products, and noise pollution problems.

### ii) Direct Flame Incineration

Whereas flares are used for destruction of waste gases which are released at concentrations above the lower limit of flammability, gases vented from the discussed processes are generally exhausted at concentrations below the lower flammable limit (around 25 % of the lower limit). At these concentrations of gases, combustion in an enclosed chamber is necessary.

There are three important parameters which influence the proper incineration of pollutants in a dilute stream:

- temperature
- time
- turbulence

First, the supplemental fuel is burned by utilizing part of the oxygen contained in the dilute fume stream to produce high temperature combustion products, above 1200 °C. At the same time, the rest of the cold fume by-passes the flame and is mixed with the combustion products (Figure 10-9). The mixing should give a uniform temperature to all fumes flowing through the incinerator. This is done as rapidly as possible without causing flame quenching so that sufficient residence time can be provided at the required temperature for the oxidation of pollutants contained in the by-passed fume. In actual incineration

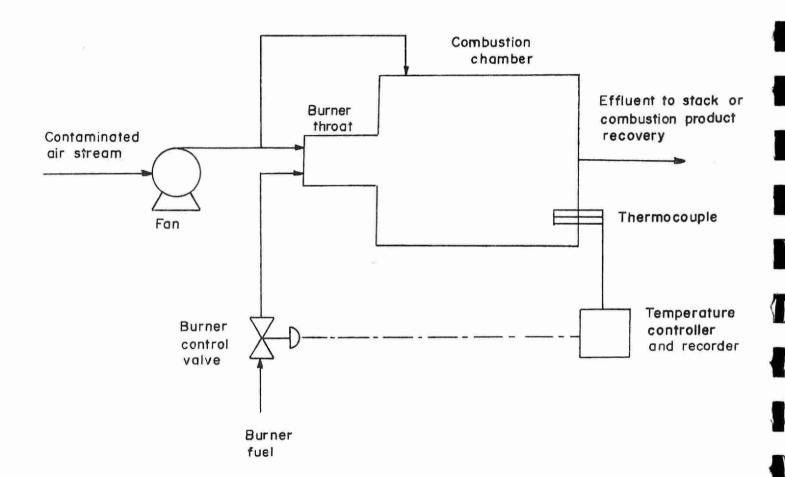


FIGURE 10-9

DIRECT-FLAME THERMAL INCINERATOR



operations, the mixing time for the gas mixture is about the same order as, or greater than, the reaction time, depending on the incinerator design. From past experience in the incineration of organic pollutants, it is reported that the destruction of most hydrocarbons occurs very rapidly at temperatures in excess of 590 °C to 700 °C. Possible exceptions are benzene derivatives, like toluene and chlorinated hydrocarbons, which are stable and require higher temperatures for complete oxidation to occur in a few tenths of a second (26). Experimental data on incineration efficiency of toluene, hexane and cyclohexane are shown in Figure 10-10. As a rule of thumb, 1000 °C and 2 seconds of retention should be satisfactory for destruction of most organic compounds including very stable chlorinated materials (25, 27).

Both the high cost and very often inadequate supply of fuel create problems in operating an incinerator. If the off-gases are not corrosive, some form of heat recovery is desirable. Two types of heat recovery equipment are usually considered:

- waste heat boiler
- feed-effluent heat exchanger

Overall thermal efficiency of 60 to 80 % may be achieved.

# iii) <u>Catalytic Oxidation</u>

This is another method of reducing the operating costs of incineration. Contact of a waste stream with a catalyst bed allows the oxidation reaction to occur rapidly at a lower temperature than that required in a thermal direct-flame incinerator (84). Five steps are

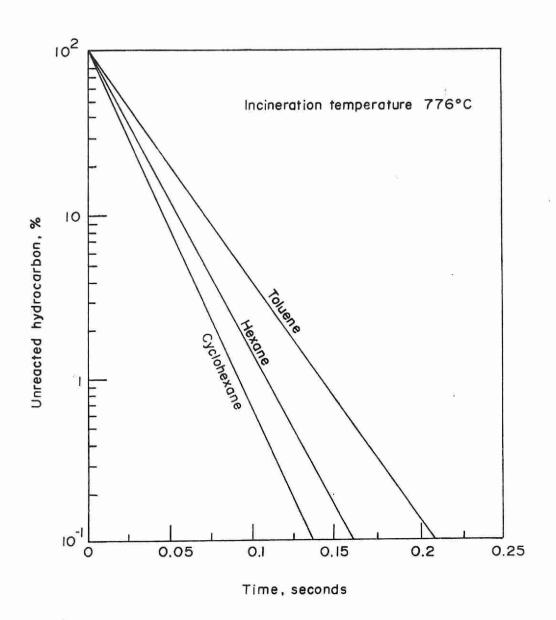


FIGURE 10-10

HYDROCARBON OXIDATION RATES IN ABSENCE OF FLAME



involved in the solid-catalyzed vapor-phase reaction:

- Diffusion of the reactants through the stagnant fluid around the surface of the catalyst
- Adsorption of the reactants on the catalyst surface
- Reaction of the adsorbed reactants to form products
- Desorption of the products from the catalytic surface
- Diffusion of the products through the surface film to the bulk vapor phase outside the catalyst

The various noble metals used as catalysts, such as platinum, palladium and rhodium, in varying concentrations, cause different reaction rates for each specific hydrocarbon. Moreover, in air pollution control, it is not practical to undertake a complex research project to develop a specific catalyst for different effluents. Therefore, commercial catalyst manufacturers have attempted to develop a universal catalyst which is effective in oxidizing a wide range of organic materials over an extended period of exposure time with minimum maintenance and replacement. Fouling and poisoning are the most frequent problems associated with the use of catalysts. One supplier (20) reports successful application of catalytic incinerators in a number of applications, including cumene manufacture. He reports catalytic ignition temperatures for some hydrocarbons. The temperature required to provide 90 % conversion will vary depending upon the contaminant concentration and the type and amount of catalyst required for the application. The catalytic ignition temperature for 90 % conversion of benzene, toluene and xylene is about 300 °C. A typical space velocity is 75,000 m<sup>3</sup> per



hour per m<sup>3</sup> of catalyst.

The catalyst is deactivated over its lifetime. The loss in activity is dependent upon the type and concentration of specific agents in the process flow in contact with the catalyst and, to a great degree, the accrual of operating time at high temperature. Loss in activity may be due to:

- sintering
- accumulation of poisons
- accumulation of products

#### 10.2.2 STORAGE TANKS

Petrochemical plants and refineries require large volume storage facilities for liquids and gases. In a modern plant, hydrocarbons are stored in totally enclosed storage vessels. Their type and design depend on the particular hydrocarbon to be stored and the process for which the storage facilities are provided.

Closed-storage vessels are constructed in a variety of shapes, but most common are cylinders, spheres or spheroids. Maximum capacities of pressure tanks are as much as 5,000 to 6,500 m<sup>3</sup> for spheres and 20,000 m<sup>3</sup> for spheroids. Spheres can be operated up to 1.4 MPa. Horizontal, cylindrical pressure tanks are designed with various capacities and pressures.

The most frequently used type of storage tank is a vertical, cylindrical, fixed-roof vessel with a conical or domed roof. They are usually vented to the atmosphere and therefore may represent a significant

source of hydrocarbon emissions. Up to 85% reduction of emissions may be achieved by installation of a floating roof or internal floating cover. These modifications eliminate breathing and filling emissions by eliminating the vapor space that exists in fixed roof tanks. The application of floating roofs or internal floating covers could be applied to all storage facilities for liquids having true vapor pressures in the range of 10 to 75 kPa. A nitrogen blanket is also used for reduction of hydrocarbon losses.

Another emission control available to fixed roof tanks is a vapor recovery unit in which the vapors are liquified and returned to storage. The efficiency of such a system is dependent on the efficiency of the vapor recovery unit (28). Because of the cost of vapor recovery units, their application is limited to the more volatile materials. Yun-Chung Sun and G.R. Killat (39) described such a system as developed by Dow Chemical. It utilizes co-polymer adsorbent beads and is claimed to be suitable for control of a number of compounds: eg benzene, styrene, toluene, methylene chloride, methyl ethyl ketone, allyl chloride, pentane, hexane and gasoline. The principle of adsorption is the same as that previously described. The authors claim 100 % control efficiency for benzene at a cost lower than conventional systems (eg refrigeration or floating roof). About 3  $\mathrm{m}^3$  of adsorbent can serve a 225  $\mathrm{m}^3$ replacement volume per day. The superficial velocity is 1 m/min and the bed capacity is about 7 % by weight, depending on temperature. The system is adaptable to tanks using nitrogen blankets.

It is estimated that 60 to 80 % of all storage facilities in Canada utilize floating roofs or equivalents to reduce the hydrocarbon losses.

Evaporative loss is a natural process whereby a liquid is

### Mechanism of Storage Losses

converted to a vapor which subsequently is lost to the atmosphere. Evaporation occurs whenever a volatile hydrocarbon is in contact with a vapor space or the atmosphere. There are six basic kinds of evaporation losses from hydrocarbon storage: breathing, standing storage, filling, emptying, wetting and boiling. Breathing losses occur when vapors are expelled from a storage tank because of temperature and/or barometric pressure changes. Standing storage losses are those resulting from leaks around latches, relief valves, and floating roof or floating cover seals. Filling losses occur when vapors are displaced to the atmosphere as a result of tank filling. Vapor expansion subsequent to product withdrawal is termed emptying loss and is due to saturation of newly inhaled air. Wetting losses are attributed to the vaporization of liquid from wetted tank walls exposed when a floating roof or floating cover is lowered by liquid withdrawal. Boiling losses occur when vapors boil off stored liquids.

The major source of hydrocarbon emissions from fixed roof tanks are breathing and filling losses, while the major source of emissions from floating roofs and internal floating covers is standing storage losses (32).

Storage emissions at petrochemical plants depend on several major factors such as liquid vapor pressure, diurnal temperature changes, schedule of tank fillings and emptyings, solar radiation absorption by the tank, and mechanical conditions of the tank (seals and fittings). The American Petroleum Institute has developed extensive formulae for calculating tank emissions (30, 31, 42). Much simplified methods are presented by other authors (32). J.W. Pervier et al (33) report losses of hydrocarbon due to storage vents in a styrene plant to be between 30 and 670 mg/kg of styrene produced. One Ontario producer (34) estimated storage and handling losses of hydrocarbons in toluene and xylene production to be around 450 mg/kg of toluene produced and 1 g/kg of xylenes respectively. R.W. Serth and T.W. Hughes (35) completed an in-depth study of air emissions from phthalic anhydride plants and estimated the storage tank emissions as follows:

o-xylene temperature	23 °C
naphthalene temperature	93 °C
ambient air temperature	20 °C
breather valves set for	1 and 1.47 KPa

ú.	Tank Capacity (m3)	Turnovers per year	Losses kg/year
o-xylene	400	230	1,830
	4,000	23	9,280
naphthalene	4,500	1	9,300
	2,250	26	10,540
	4,500	13	14,430

## 10.2.3 FUGITIVE SOURCES

One of the largest, yet most difficult to control, category of hydrocarbon emissions from petrochemical processes is fugitive sources. Fugitive sources include pump seals, relief valves, pipeline valves, sampling and blind changing (32).

Pumps and compressors required to move liquids and gases can leak products at the point of contact between the moving shaft and the stationary casing. If volatile, the leaked product will evaporate to the atmosphere. The two types of seals that are commonly used in industry are packed seals and mechanical seals. The latter ones are more expensive but reduce losses significantly, usually by 90 % (32).

For safety and equipment protection, high pressure vessels are commonly equipped with <u>relief valves</u> to vent excessive pressure.

Corrosion may cause pressure relief valves to reseat improperly, creating a potential source of hydrocarbon leaks and emissions. Surveys indicate (32) that hydrocarbon leaks from relief valves on process vessels average 1.3 kg/day-valve and from relief valves on pressure storage tanks average 0.25 kg/day-valve. Proper maintenance should greatly reduce these emissions.

Under the influence of heat, pressure, vibration, friction, and corrosion, valves and flanges generally develop leaks. The hydrocarbon emissions from these leaks depend on both the volatility of the product and the leak rate. Tests of numerous valves indicate average hydrocarbon emissions of .08 kg/day-valve (32). Again a good maintenance schedule should reduce the emissions from valves and flanges.

The operation of process units is constantly checked by routine analyses of feedstock and products. To obtain representative samples for these analyses, <u>sampling lines must be purged</u>, resulting in hydrocarbon vapor emissions.

There are two important factors in the control of fugitive emissions - design and maintenance. Good design, however, requires good maintenance in order to be effective. The most effective design measure to date has been the increased use of flares. The trend over the years has been to tie in all pressure-relief devices to a flare. An alternative means of controlling slowly leaking safety valves (that do not vent to a flare) is to install rupture discs ahead of the valve.

Dual sets of seals can be installed on pumps and compressors, with provision made for venting the vapors that leak past the first seal into a vapor-recovery system or a flare. Mechanical seals are gradually replacing packed seals.

Two major studies are underway to determine the fugitive hydrocarbon emissions:

- California Air Resources Board: Hydrocarbon Project (40)
- Radian Corp. for US EPA under Contract No. 68-02-2147 (41)

  A study being undertaken by the Americal Petroleum Institute should also provide a method of estimating fugitive emissions with specific emphasis on storage facilities (42).
- D.D. Rosebrook (37) summarizes some inexpensive and simple methods for reduction of fugitive emissions:

- replace seals, substituting mechanical seals for packed seals
- replace packing in valves, perhaps substituting packing materials or type
- replace gaskets, perhaps substituting a different material
- clean and reseat pressure-relief devices and tie them into a flare system
- cover drains
- substitute units less susceptible to fugitive emissions,
   such as exchanging a barometric condenser for a surface
   condenser
- install more modern pumps, valves, compressors, etc.

#### 10.3 WASTE WATER EFFLUENT CONTROL

With the advent of plastic materials replacing many items in all areas of domestic, commercial and industrial applications, new problems of pollution are being developed. Various synthetic compounds are used or produced in the petrochemical industry, plastics manufacturing, solvent production, degreasing operations, textile mills, dyes and paint manufacturing, insecticides production, etc. The waste materials being generated create new challenges to technology for their disposal. One major source of pollution is the process plant itself. However, pollution could be caused by any accidental release during packaging, transport, use, and/or disposal. Many aromatic and chlorinated aromatic hydrocarbons are compounds which are very persistent in the environment.

Until recently, the approach to control of toxic pollutants in industrial waste water effluents has been governed by a set of regulations that covers the discharge of all pollutants. Even though the knowledge on toxicity of individual pollutants has improved, there is still much to learn. In many cases, data on the monitoring of discharges, analytical capabilities, toxicity of pollutants, and their persistence and degradability are incomplete or missing.

The type of compound, its physical and chemical properties, and their interrelationships will greatly affect its behaviour and fate in the environment. The most important properties from a waste water

treatability viewpoint are:

- solubility in water
- toxicity and other adverse effects on fish
- toxicity to human or animal life (See Section 13)

## 10.3.1 SOLUBILITY OF ORGANIC COMPOUNDS IN WATER

Table 10-1 shows the solubilities of individual compounds in water at 25  $^{\circ}$ C. For more detailed information on the physical and chemical properties of the compounds of interest here see Section 7.

Most of the chlorinated hydrocarbons, and benzene, toluene, and styrene are highly soluble in water. Naphthalene, cumene and p-dichlorobenzene are rather insoluble in water. However, all of these compounds are highly soluble in a number of solvents or oils and their solubility in waste water could be, therefore, much higher than in pure water. Solubility decreases with decreasing temperature.

#### 10.3.2 TOXICITY TO FISH

The concentration found to be toxic to fish are listed in Table 10-2.

Naphthalene and dichlorobenzene are the most toxic compounds to fish (toxic at 5 ppm). Other compounds are generally toxic at about 20 ppm.

The compounds seem to have a narcotic effect on fish. Prior to death the fish swims wildly and erratically, but death is delayed for some time after equilibrium loss is first produced and after the fish

## TABLE 10-1

# SOLUBILITY OF ORGANIC COMPOUNDS IN WATER AT 25 °C (46-49, 55)

COMPOUND	SOLUBILITY IN WATER g/1
Benzene	1.860
Toluene	0.500
Xylene	0.130
Naphthalene	0.040
Ethylbenzene	0.175
Styrene	0.320
Cumene	0.039
Chlorobenzene	0.448
Dichlorobenzene	
o- m- p-	0.145 0.123 0.079
Methyl Chloride	4.800
Methylene Chloride	20.000
Chloroform	8.220
Dichloroethane	
1,1- 1,2-	5.500 8.690
Trichloroethane	
1,1,1- 1,1,2-	4.400 4.500
Tetrachloroethane	
1,1,2,2-	2.900
Dichloroethylene	
1,1- cis 1,2- trans 1,2-	0.400 3.500 6.300
Trichloroethylene	1.100
Perchloroethylene	0.150
Chloroprene	N/A



TABLE 10-2

TOXICITY OF AROMATIC COMPOUNDS TO FISH

COMPOUND	CONCENTRATION TOXIC (ppm) TO FISH	REFERENCE
benzene	11 22 35	50 51 53
toluene	61 24 47 21	53 51 53 51
xy lene	47 21	53 51
naphthalene	4-5 3	53 52
ethylbenzene	29	51
styrene	22	51
cumene	N/A	
chlorobenzene	20	51
dichlorobenzene	5	53

N/A - Not available

is immobile with only a slight twitching of the gill covers and pectorial fins.

Static bioassay tests, except those by Meyerhoff (50), and different kinds of fish were used in the tests. Since many of the compounds are highly volatile (eg benzene, toluene), the toxic concentrations could be much lower in a continuous bioassay.

"Bioaccumulation" of benzene, toluene, chlorobenzene, p-dichlorobenzene and naphthalene in different parts of the fish body has been determined by Neely (54), Chiou et al (55), Neff (56) and Lee et al (57). Bioaccumulation is defined as the ratio of the concentration of the chemical between muscle and the exposure water when measured at equilibrium. Naphthalene accumulated in fish tissue to the highest concentration. A biomagnification factor of 2.3 for naphthalene and up to 26.7 for trimethylnaphthalene has been found.

Benzene, toluene and xylene have been found in muscle and liver from fish taken close to petroleum and petrochemical waste water effluents by Ogata et al (58). The fish were offensive smelling and gas chromatographic data indicated that the offensive odor was probably due to toluene contained in petroleum industrial wastes.

#### 10.3.3 FREE OIL REMOVAL

The choice of treatment processes for water effluents depends on the concentration of these chemicals in the water, and the nature of other contaminants which make up the total organic load in the effluent.

Large amounts of dispersed aromatic hydrocarbons and other oils



can be separated from waste water by processes generally used for removal of free oil and solids, as described by Thompson et al, 1972 (59), Gardner, 1972 (60), Quigley and Hoffman, 1967 (61), Taylor, 1973 (62), and Grutch and Mallatt, 1976 (63). By using different processes, different effluent quality could be achieved:

## Effluent with >200 ppm 0il

Effluent of this quality can be expected from gravity oil-water separators. The separators may have a variety of designs and sizes according to various oil densities. Gravity oil separators will not remove emulsified oil. This separation is usually satisfactory in a system with secondary treatment.

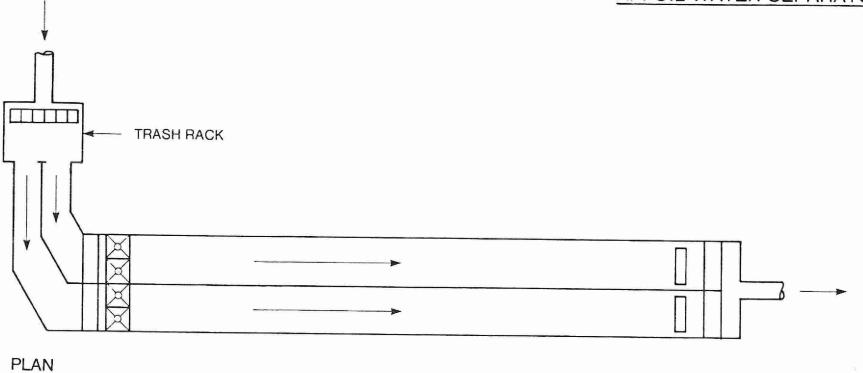
## Effluent with 50-200 ppm 0il

A well designed and carefully operated American Petroleum Institute (API) separator (Figure 10-11) can produce effluent of this quality. The addition of flocculant should be considered, particularly if a significant amount of oil is emulsified, or if an improvement in solids separation is desirable. Better quality effluent may be obtainable by using a separator larger than API design. The API separator performance varies widely and the minimum effluent oil content that can be expected is about 50 ppm.

## Effluent with 10-20 ppm 0il

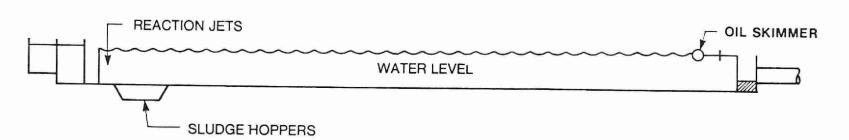
Treatments such as induced air flotation, dissolved air flotation and filtration can produce a high quality effluent with less than 20 ppm oil.

# API OIL WATER SEPARATOR





UNITED TECHNOLOGY and SCIENCE INC.



**ELEVATION** 

Induced air flotation (IAF) is a process in which air is dispersed through the waste with agitators, or venturi nozzles are provided to entrain air and disperse it into the water, to float suspended oil and solids to the surface, where the froth is removed by paddle skimmers.

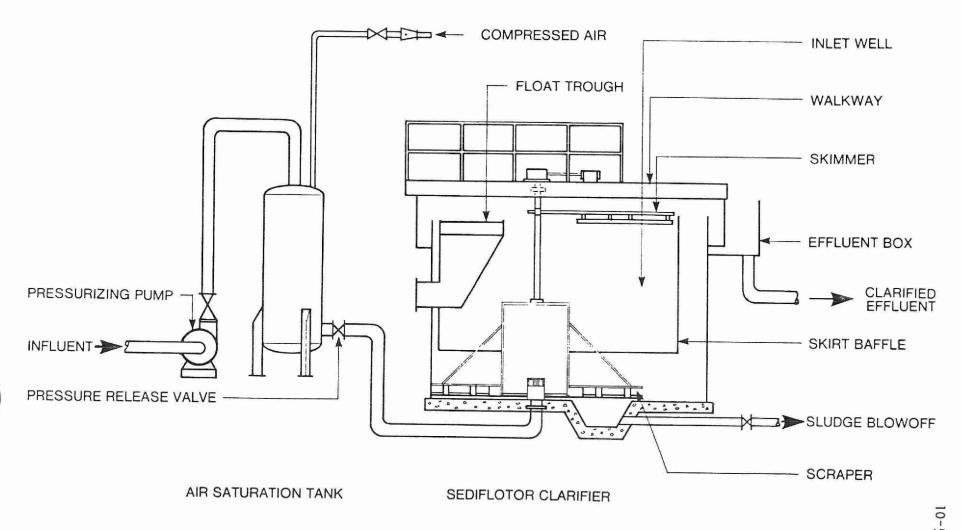
In dissolved air flotation (DAF) (Figure 10-12), air is introduced into water under pressure so as to increase its solubility. When the pressure is reduced, there is an immediate release of fine bubbles of air which rise to the surface. There are many different flow arrangements and types of equipment for carrying out this operation.

Granular media filtration (Figure 10-13) is used for oil and solids suspension separation. Filter media include beds composed of sand, sand/coal, sand/coal/garnet and other minerals and synthetic materials. They can operate under gravity or pressure.

The dual media filters (DMF) (sand/coal) are the most widely used. Normal operation involves a downward flow through a bed of increasingly smaller pore size media until the pressure drop due to clogging or breakthrough of oil and solids increases to a predetermined level. The filter is then cleaned by backwashing which includes air scrubbing, reversed fluidization, and a surface wash.

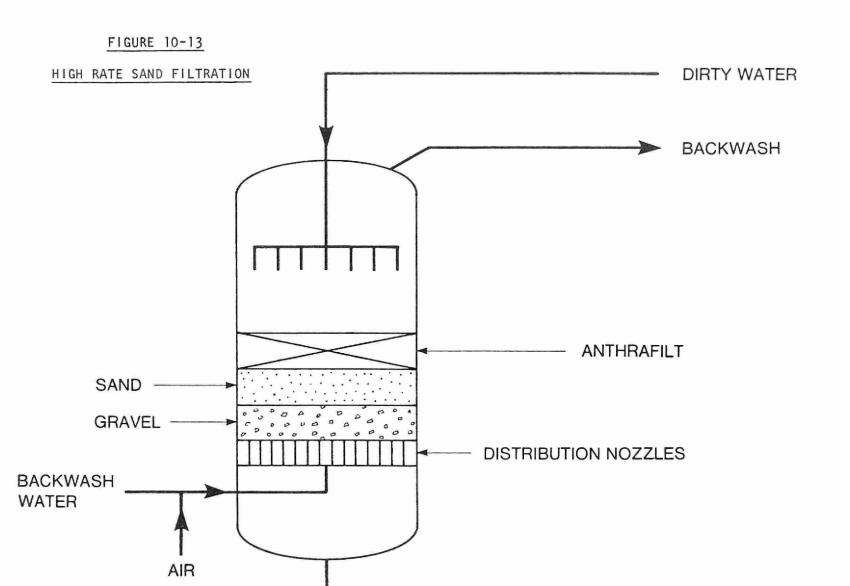
The performance of all three units (IAF, DAF, DMF) is improved by using an additive. DAF and DMF usually produce an effluent of superior quality to IAF. For oil removal, DAF and DMF seems to be comparable, but suspended solids removal is much better by filtration.

## FIGURE 10-12 DISSOLVED AIR FLOTATION



FILTERED WATER





Since DAF is usually cheaper than filter installation, it would normally be the process of choice for oil removal alone. However, filtration usually gives better effluent quality on waste water containing large amounts of oil. The filter backwash water requires more treatment than DAF sludge.

### Effluent with <10 ppm 0il

After pretreatment to remove gross amounts of oil, effluents with less than 5 ppm of oil can be obtained from treatment such as biological oxidation or activated carbon adsorption. Studies show that these processes give excellent removal of soluble oil. When activated carbon adsorption or biological oxidation treatments are used, a major cost saving results from optimizing the pretreatment steps.

#### Other Treatment Methods

Concentrated solutions of toxic hydrocarbons can be disposed of by incineration (see Section 10.4) or wet-air oxidation. Many streams can be recycled to the reactors where they are converted into useful products. Another common practice is product integration. Products are recovered from the waste stream for reuse in a different plant at the same site or are shipped to another plant which has a use for them.

#### Wet Air Oxidation

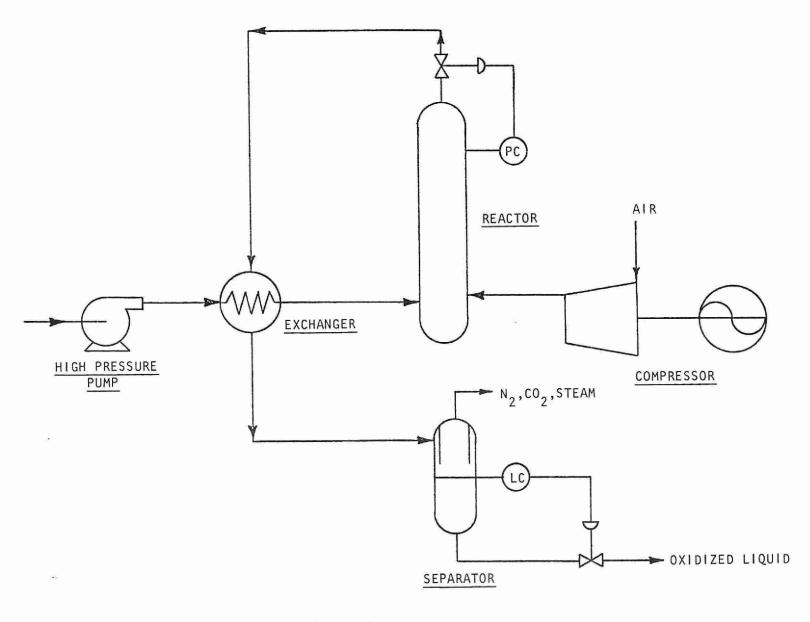
This process is suitable for the oxidation of waste waters which have a concentration of oxidizable material of 2-20 % by weight in water. In the process, the organic matter is oxidized by air or oxygen at elevated temperature and pressure. The typical operating



conditions are 230 °C and 4.1 MPa. Good removal of dangerous toxic and obnoxious wastes and an efficient recovery of energy from relatively dilute waste streams is claimed, Ontario Research Foundation, 1977 (83).

Figure 10-14 shows the flow scheme. Waste water is pumped through the heat exchanger into a reactor. The reaction between the oxidizable material and the air proceeds autogenously. Spent air, carbon dioxide and steam are separated from the treated waste water. During the oxidation process, high molecular weight compounds are oxidized to lower molecular weight compounds which are easily biodegradable. The BOD of waste increases substantially. The degree of oxidation is a function of the reaction temperature and residence time. Operating pressure depends on the temperature and the concentration of organics.

An attractive treatment is combined wet air oxidation - biophysical treatment, Figure 10-15 (85). In this process, the organics are first partially oxidized by wet air oxidation. In the aeration basin, the waste is contacted and adsorbed on powdered activated carbon and biooxidized. Carbon and the biosludge are separated from waste water in the clarifier, returned to the aeration basin or thickened and regenerated by wet air oxidation - regeneration. Wet air oxidation is an effective and proven technology for regeneration of powdered activated carbon. Larger capacity wet air oxidation systems can be used for both oxidation treatment of waste water and regeneration of carbon. Alternatively, two separate wet air oxidation systems may be installed. An advantage of this treatment is the elimination of sludge disposal.







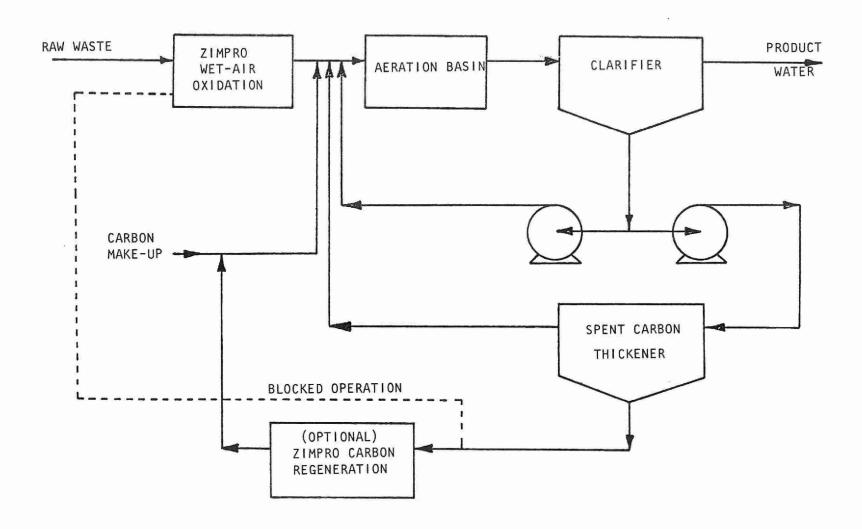


FIGURE 10-15. WET AIR OXIDATION - BIOPHYSICAL TREATMENT

Biomass associated with the carbon is destroyed during the regeneration process. The wet air oxidizes the remaining adsorbed organics and the biomass is solubilized and returned to the aeration basin in a biodegradable form.

#### 10.3.4 SOLUBLE OIL REMOVAL

There are two possible choices for the removal of soluble aromatics from water effluents - biological oxidation or physico-chemical treatment. The type of treatment is selected according to the nature of the contaminants.

The organic load in waste water effluent has been measured by different tests. These tests are:

- BOD Biochemical Oxygen Demand is a measure of the amount of oxygen required for the complete decomposition of organic matter by microbes which grow and oxidize the organics aerobically. Historically, BOD5 (fiveday BOD) tests have been used, but also BOD10, BOD20 and BOD-ultimate are used with more difficult to oxidize wastes.
- COD Chemical Oxygen Demand is a measure of the oxygen equivalent of the materials present in waste water which are subject to oxidation by potassium dichromate under acid conditions. Some aromatic hydrocarbons are not oxidized in this test. Interferences result from chlorides and inorganic reducing agents.

TOC - Total Organic Carbon is the amount of carbon in the organic matter as measured by an automatic total carbon analyzer.

Biological oxidation treatment is efficient if there is a similarity between COD or TOC and BOD. Very low BOD and high TOC indicate non-biodegradable wastes or the presence of toxic pollutants. Domestic sewage has approximately BOD $_5$ /TOC  $\simeq 1.85$ , BOD $_5$  is  $\sim 77$  % of ultimate BOD and ultimate BOD is  $\sim 90$  % of the theoretical oxygen demand. Generally, the biooxidizable waste has BOD $_5$ /TOC = 1.35 -2.6. Typical petrochemical and chemical waste water effluent will consist of biodegradable and non-biodegradable organics.

The bacterial oxidation of simple aromatic and polycyclic aromatic hydrocarbons has been reported in a number of scientific publications (64-72) and a well defined pathway for bacterial degradation of the aromatic nucleus was proposed by Marr and Stone, 1961 (67) (see Figure 10-16). Oxidation of aromatic hydrocarbons appear to be more difficult and much slower than oxidation of aliphatic hydrocarbons. For example 3.5 % of benzene was found to be oxidized in 6 hours and only 13 % was oxidized in 192 hours by acclimatized activated sludge (71).

The first steps in the oxidation are apparently unique and can be carried out only by a limited number of strains of soil bacteria (Pseudomonas, Achromobacter, Micrococcus, Vibrio, Nocardia). Studies by Tabak, 1964 (65) show that bacteria adapted to one aromatic compound (phenol) can oxidize related compounds (benzene). In any case, the adaptation of bacteria to an aromatic compound substrate is a slow process.

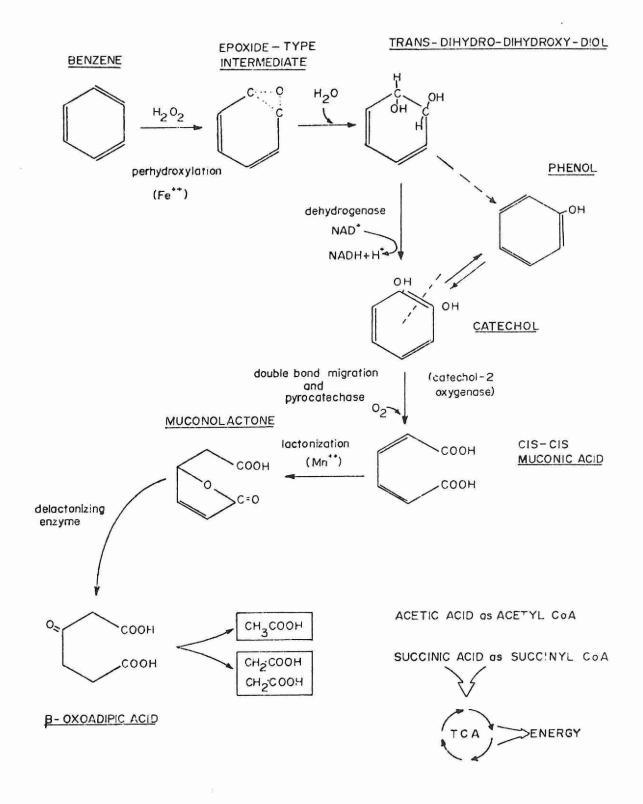


FIGURE 10-16

## MICROBIAL OXIDATION OF AROMATIC COMPOUNDS



## 10.3.4.1 HIGH CONCENTRATION EFFLUENTS

Distillation or stripping are the methods used for

Waste streams with a soluble organics concentration between 0.5-5 wt. % present a problem, since they are on the borderline between levels normally associated with recovery in the process plant and levels associated with waste treatment. Although conventional chemical engineering techniques such as distillation, evaporation, stripping and extraction can be used to reduce concentration of pollutants in waste water, the capital costs and energy requirement vs. desired pollution reduction rise exponentially. Membrane separation processes can theoretically produce highly concentrated streams. Perhaps development of efficient membranes will eventually allow these techniques to be used more widely. Pretreatments such as equalization, mixing, pH adjustment, flocculation/coagulation, flotation, filtration and oil separation are commonly used to prepare waste water for further treatment. Distillation or stripping can separate compounds with appreciable vapor pressure into a more concentrated stream (81). Both processes are energy intensive. They are more expensive than evaporation. Evaporation is a widely used technique for concentrating waste water streams containing compounds of negligible vapor pressure. The fouling tendencies of waste waters often present problems. Extraction: Solvent extraction is an attractive and economically promising treatment for waste waters where organic load is high, recovery of organic solutes is desirable, or where the water presents special problems for biological treatment. Extraction is preferred for substances of relatively low solubility in water and sufficiently high solubility in the solvent.

pollutant separation from the loaded solvent (Figure 10-17).

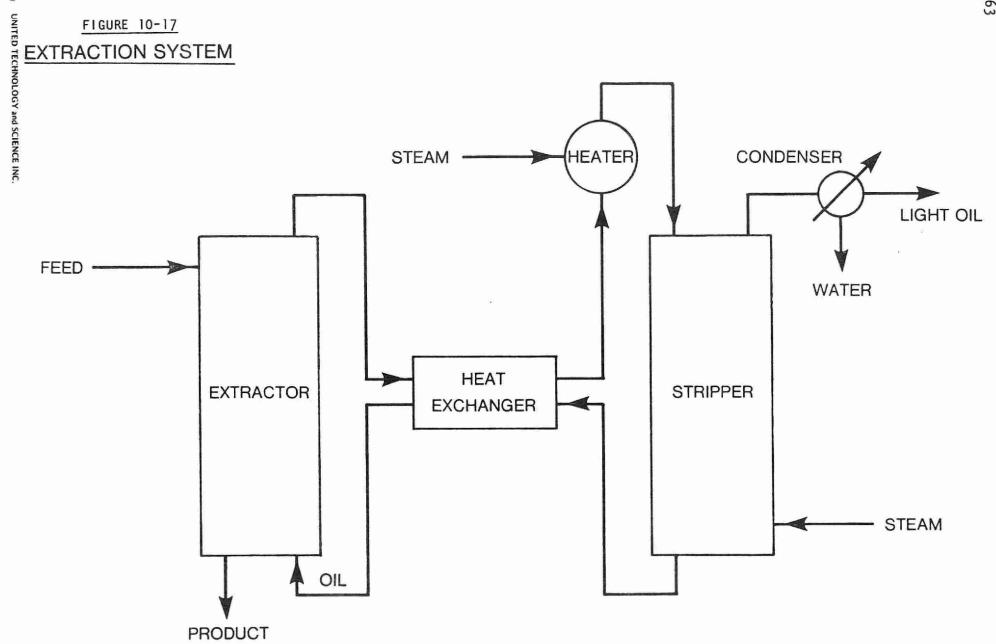
In the extraction process the choice of solvent is important. If the solvent does not have to be regenerated, the selection is not difficult. The most important considerations are:

- 1) Partition coefficient  $K_d$  (ppm pollutant in solvent/ppm pollutant in water). Use of the value  $K_d$  at infinite dilution for each pollutant independently is normally satisfactory.
- 2) The solvent should be highly insoluble in water.
- 3) The solvent density should be very different from that of water.
- 4) The normal boiling point of the solvent should be higher than that of the pollutant for recovery of the pollutant as a distillate. When choosing a volatile solvent, the heat economy is very important. During the distillation, all of the volatile solvent must be boiled off and then condensed.

In a set of small pilot plant experiments, industrial waste water samples were tested for pollutants extraction (89):

Lube oil refining waste water containing 25-40 ppm acetone, 108-232 ppm methyl ethyl ketone (MEK), 37-107 ppm benzene, 17,000-23,200 ppm phenol and 1200-2660 ppm o-cresol was studied for extraction with the volatile solvent, isobutylene, and with the polar solvent, n-butyl acetate. The removal of





approximately 51 % acetone, 49 % MEK, 89 % phenol, 95 % o-cresol and 75 % benzene was obtained.

Ethylene quench waste water produced in a naphtha pyrolysis olefins plant, containing 71-81 ppm benzene, 40-44 ppm toluene-, 34-40 ppm xylenes, and 67-68 ppm phenol was treated with the volatile solvents, isobutane and isobutylene. The removal of individual pollutants was 97 % for benzene, 96 % for toluene, >97 % for xylenes and 3 % for phenol.

The waste water from an oxychlorination plant which produces ethylene dichloride contained 1.5-5.8 % HCl, 14,100-16,900 ppm chloral, 1500-3360 ppm ethyl dichloride, 290-520 ethanol, 0-100 ppm acetaldehyde and 0-300 ppm monochloro-acetaldehyde. In a dual solvent process using 2-ethyl hexanol and isobutane solvents, removal of ethylene dichloride was more than 99 %.

The waste water from a plant manufacturing styrene contained 345 ppm benzene, 170 ppm ethylbenzene and 10-20 ppm styrene.

The solvent, isobutylene, removed the dissolved aromatics very effectively. The percentage removals observed were:

97 % benzene, 97 % ethylbenzene and >93 % styrene.

#### Membrane Processes

Membrane processes can be used for concentration and separation of toxic organics from chemical effluents. They require less energy and are compact. However, difficulties have been experienced from membrane

plugging and in maintaining membrane efficiency. More use can be expected with improvements in membranes.

#### Reverse Osmosis

In this process, the contaminant is physically separated from the water by circulating the solution at high pressure over the surface of a semipermeable membrane. The membrane will permit only water molecules to pass through, being impermeable to contaminant molecules. The degree of contaminant removal and the flux of purified water permeating through the membrane depends on the type of contaminant, the concentration membrane material, the temperature and the pressure head. The pressure head at equilibrium is defined as the osmotic pressure. If an external pressure is applied on the side of greater concentration, water will flow in the opposite direction; this is defined as reverse osmosis. The contaminant will concentrate in the reject stream. Extensive pretreatment of the waste water is necessary for solids and oil removal. A number of soluble organics will not only foul the membranes, but in high concentrations they will also partially dissolve it.

Thirteen pesticides, including chlorinated hydrocarbons and two metabolites of pesticides, were tested for removal by two types of the reverse osmosis membranes (eg.cellulose acetate (CA) and cross-linked polyethyleneamine NS-100) (88). With each membrane, the rejection of pesticides was better than 99 %. A considerable amount of pesticides, however, adsorbed on the membrane material. Removal of more polar pesticides was less satisfactory than removal of nonpolar pesticides

(such as chlorinated hydrocarbons).

#### Dialysis

This is a process which separates various compounds in solution on the basis of their molecular dimensions and the difference in chemical activity of the transferred compounds on the two sides of a membrane. The driving force is the concentration gradient, which means that with the passage of water through the membrane, the efficiency of the separation process decreases. Dialysis can be a suitable means of separation for low concentration contaminants (less than 0.1%).

Success in treating concentrated acid waste streams and good recoveries of different acids are claimed.

#### 10.3.4.2 LOW CONCENTRATION EFFLUENTS

The treatments available for removal of toxic organics from low concentration waste water streams are: 1) biological oxidation, 2) activated carbon adsorption, 3) biophysical treatment, 4) chemical oxidation, 5) adsorption on polymeric adsorbents and 6) catalytic reduction.

#### 10.3.4.2.1 BIOLOGICAL OXIDATION

The difficulties in oxidizing aromatics indicate that in biooxidation treatment a longer contact time of the substrate with microbes
(sludge) is preferred and therefore, activated sludge, aerated lagoons
and ponds appear to be more suitable than, for example, a trickling filter
(90).

In biological treatment, organic matter is largely oxidized to carbon dioxide and water, with some being used in the synthesis of

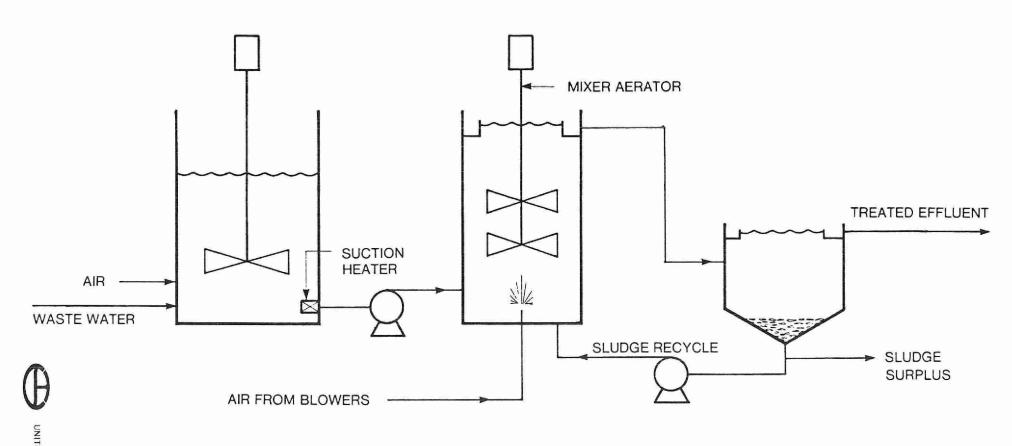


new cells. The start-up times of biological treatment processes for systems handling organic chemical wastes are longer than for systems handling municipal wastes. Because of the extremely unfavorable reaction kinetics, staging is a common practice. For example, an aerated lagoon preceding a completely mixed activated sludge or an aerated stabilization basin preceding pure oxygen activated sludge.

The system requires food (waste water) and oxygen (dissolved oxygen from aeration). The microorganisms feed on the organic matter in waste water, thereby reducing the strength (BOD) of the waste. The proper operation of an activated sludge plant requires that the design F/M (food to microorganisms) ratio be maintained. The F/M range for conventional activated sludge is 0.25-0.35 and, for extended aeration, 0.02-0.04. The mass of microorganisms varies from 2000-5000 mg/l of mixed liquor suspended solids (MLSS). Figure 10-18 shows the activated sludge treatment process flowchart. After equalizing in the equalizing tank, the waste water is contacted with sludge in the aeration tank. In the sedimentation tank, the sludge is separated from the waste water, part of the sludge being returned to the aeration tank. Surplus sludge is wasted.

Where a high rate of organics removal is required, some type of activated sludge unit is the most practical solution. All types of high rate activated sludge units are sensitive to shock loads and therefore must be protected. The usual method is to use equalizing tanks for the feed.

ACTIVATED SLUDGE TREATMENT



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Activated sludge treatment is not recommended for wastes containing a large concentration of highly volatile aromatics (benzene, toluene), due to the danger of creating an odor problem. Also, if the sludge is not enriched with the aromatic hydrocarbon oxidizing microbe, the compound could go through the treatment unchanged and then need to be removed in a polishing treatment step.

#### Activated Sludge Process

The activated sludge process may be briefly described as a system in which a large number of biological organisms are maintained and continuously circulated so as to be in constant contact with the organic waste water in the presence of oxygen.

#### Trickling Filter

This is a bed filled with rocks or synthetic media, 1-5 m deep.

The media provide surfaces for biological sludge growth. The organic material is oxidized as the water flows through. The organic load ranges from 2.3-11.4 kg for high rate filters.

The advantage of this process is the ability to cope with shock loading. In general, materials toxic to bacteria in the activated sludge will be toxic to a trickling filter. It is not recommended that a trickling filter be used as a single stage treatment but that it be installed as a roughing device or first stage biological treatment.

#### Aerated Lagoon

This is a basin 2-6 m deep in which the incoming waste water is contacted for long periods of time with a dispersed biological growth.

Aeration is provided by mechanical or diffused aeration equipment. In

the aerated lagoon for treating synthetic organics at a Union Carbide Plant, the reduction of naphthalene, styrene and toluene was 70-90 % and benzene 9-100 %. The plant operates with 74-90 kg/day/ 1000 m<sup>3</sup> BOD load and 155-181 kg/day/1000 m<sup>3</sup> COD load and 66 hours retention time. The overall removal of BOD was ~50 % and of COD ~40 %. It is recommended that an aerated lagoon be used as an equalization tank or a polishing pond.

## Oxidation Ponds

These are large shallow ( $\sim$ 1.2 m) basins. Aeration is accomplished by natural surface reaeration and algal photosynthesis. Retention times in the ponds range from a few days to 3 months. Ponds are used for polishing the effluent from biological waste treatment processes. It is recommended that typical BOD loadings ranging from 9-45 kg BOD $_5$ /acre/day for raw waste and 4.5 kg BOD $_5$ /acre/day for polishing waste effluents be used. Reported BOD removal efficiencies are 60-90 %.

#### 10.3.4.2.2 ACTIVATED CARBON ADSORPTION

Activated carbon adsorption is the most up-to-date method and is receiving more and more attention from municipalities and industries for use in the removal of organic compounds that are not readily biodegradable, are toxic to fish, or produce taste, color or odor in waste waters.

Activated carbon has a highly porous structure of very large surface area, 500 to 1200 m $^2/g$ , which provides many sites upon which adsorption of molecules can take place. The average pore size is small, around 3  $\mu$ m, and the distribution of pore sizes is quite wide. The adsorption of organics is a results of physical and chemical forces. Physical adsorption

results from molecular condensation in the capillaries of the carbon particle, and chemical adsorption results from a chemical bond between the carbon surface and organic molecule. The rate of adsorption is controlled by the rate of diffusion of the soluble molecules into the capillary pores of the carbon particles. An adsorption equilibrium is established when the concentration of contaminant remaining in solution is in a dynamic balance with that at the surface. Adsorption capacity will increase with increasing concentration of contaminant in solution and with its decreasing solubility in solution. The adsorption phenomena is usually expressed by the Fruendlich isotherm:

X/M = kC<sup>1/n</sup> X - weight of contaminant adsorbed
M - weight of adsorbent (carbon)
C - concentration of contaminant remaining in
solution

k,n - constants depending on temperature, adsorbent and the substance to be adsorbed.

Both organic and inorganic compounds can be adsorbed. Adsorbability of different organic components varies widely with molecular size, structure, branching, solubility, polarity, pH and other factors. Table 10-3 shows the influence of molecular structure and other factors on adsorbability, as presented by Ford, 1972 (76). Generally, nonpolar aromatic hydrocarbons of low molecular weight, such as benzene, are highly adsorbable on carbon. The aromatics are capable of  $\pi$ -bonding

#### TABLE 10-3

## INFLUENCE OF MOLECULAR STRUCTURE AND

## OTHER FACTORS ON ADSORBABILITY

- Aromatic compounds are generally more adsorbable than aliphatic compounds of similar molecular size.
- 2. Branched chains are usually more adsorbable than straight chains.
- 3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similarincreases do not occur when introduced into higher fatty acids.
Double bonds	Variable effect.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

- An increasing solubility of the solute in the liquid carrier decreases its adsorbability.
- Generally, strongly ionized solutions are not as adsorbable as weakly ionized ones; ie, undissociated molecules are in general preferentially adsorbed.
- 6. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.
- 7. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute-carbon chemical bonds being formed, making desorption more difficult.



with the surface of the activated carbon, which has been found to be aromatic in nature.

There is very little information in the literature on the adsorbability of specific compounds. The most comprehensive study on adsorbability of pure compounds from ten functional groups commonly found in petrochemical effluents was given by Giusti et al, 1974 (74). In this study, the removal of benzene was 95 %, toluene 79.2 %, ethylbenzene 84.3 % and styrene 88.8 %. Ninety-five percent removal of benzene was also found by Scherm and Lawson, 1976 (73). High adsorbability was predicted for toluene and chlorobenzene by Rizzo and Shepherd, 1977 (75).

The effectiveness of activated carbon adsorption treatment for industrial waste waters is usually measured by removal of organics (TOC), COD, color or toxicity. Waste water effluents often contain a number of contaminants and are too complex to characterise. Hagar, 1973 (77) surveyed 222 adsorption isotherms of waste water from 68 industries. The results of this survey show that activated carbon adsorption reduced TOC by more than 90 % in 10 samples, 85-90 % in 29 samples and less than 85 % in 53 samples. The TOC was used in these studies because it is a better measure of adsorption performance than COD or BOD. Chemical clarification, oil flotation and filtration were common pretreatment processes.

Experience shows that not all organics adsorb completely in a multicomponent system such as petrochemical effluent. While aromatics are reported to be relatively efficiently adsorbed, Scherm and Lawson, 1976 (73), some low molecular weight oxygenated organics have only

limited adsorbability. Competition for adsorption sites and mutual solubility may result in the leakage of some aromatics in the effluent. Also, since adsorption on carbon is dependent on the dynamic concentration equilibrium, unloading and leakage are likely to occur in the periods following extremely high concentrations of organics in the feed to the carbon bed (eg spills).

Fixed-bed and expanded-bed carbon adsorbers are commonly used for continuous treatment. Waste water is applied to the beds at rates generally ranging from 2 gpm/ft $^2$  and 8 gpm/ft $^2$  (81-326  $\&/\min/m^2$ ). Lower flow rates are used in downflow gravity packed beds. Higher flows are used in expanded-bed upflow adsorbers. An essentially equivalent adsorption efficiency is obtained from equivalent contact time. Contact times employed are in the range of 30 to 60 minutes on an empty bed basis.

By passing waste water upward through the bed of carbon at velocities sufficient to expand the bed, problems of fouling, plugging and increasing pressure drop are minimized.

Biological growth on the surfaces of the carbon can present some problems in packed bed adsorbers. Effective control of biological growth can be accomplished by regular chlorination of the feed to the adsorbers or by chlorination during backwashing. Anaerobic conditions and H<sub>2</sub>S production are controlled by aeration of the feed. Regular backwashing and air scouring should be provided to remove solids and biological growth. Granular carbon has been used in most systems because of the relative ease of handling and regenerating.

Due to the complexity of industrial effluents and the high cost of activated carbon adsorption treatment, the feasibility of its use should be determined by both carbon adsorption isotherm and continuous flow pilot plant simulation tests.

#### Carbon Adsorption Isotherm

To determine the isotherm, contaminanted water is contacted with a series of known weights of pulverized carbon and agitated at a constant temperature. After the adsorption equilibrium is reached, the carbon is removed and the residual concentration of contaminants measured. The test data are plotted on a log-log scale representing the isothermal relationship between contaminant concentration and carbon equilibrium capacity. Figure 10-19 shows different types of Fruendlich isotherms, Ford, 1972 (76). The isotherm is used to estimate carbon capacity. However, the data should not be used for design purposes since the isotherm represents only an ideal system.

#### Pilot Plant Tests

Continuous pilot plant tests, preferably on site, are necessary to investigate the effect of the variability of plant conditions, spills and possible leakage of contaminants from carbon columns. Columns 2-8 inches (5-20 cm) in diameter and 5-8 feet (1.5-2.4 m) in height, usually connected in series (upflow or downflow) are used in the tests (Figure 10-20). Facilities for backwashing should also be provided.

Pilot plant tests determine the contact times necessary for contaminant removal, the amount of carbon consumed per unit volume of liquid treated (service time of the bed), and the required regeneration frequency

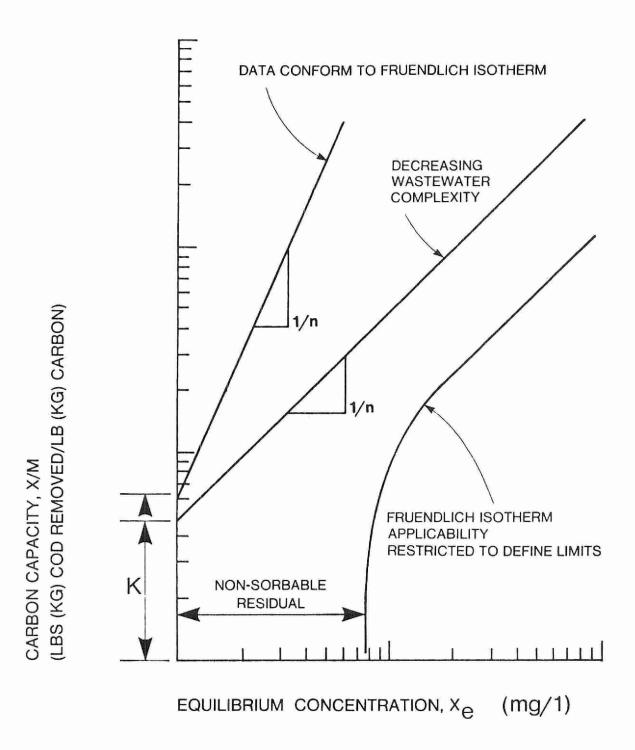


FIGURE 10-19



backwash inlet

control valve

FIGURE 10-20
SCHEMATIC OF PILOT PLANT FOR CARBON ADSORPTION TESTING

for carbon. Long carbon contact time and low surface velocity increase the effluent quality and carbon bed service life.

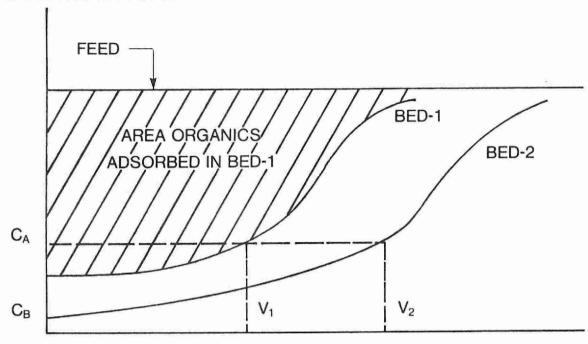
From the columnar study a breakthrough curve is constructed and all necessary data calculated. Figure 10-21 shows an ideal breakthrough curve (water of a constant composition) and Figure 10-22 shows experimental breakthrough curves for a system with two beds in series, Scherm and Lawson, 1976 (73).

There are four options regarding the handling of carbon after it has been exhausted:

- a) Throwaway Carbon: Virgin carbon is charged into the adsorbers. When it becomes exhausted it is removed and disposed of by landfilling.
- b) Offsite Reactivation: Carbon is shipped to an offsite reactivation facility for thermal reactivation.
- c) Onsite Reactivation: A multi-hearth furnace or rotary kiln is used to thermally reactivate spent carbon (Figure 10-23).
- d) Adsorption Service: Service by carbon producing company for adsorption equipment and carbon handling.

Addition of powdered activated carbon improves activated sludge treatment because of the carbon adsorptive and physical properties, Perrotti and Rodman, 1973 (78), Davis, 1977 (79), DeJohn and Adams, 1975 (80). Organics and oxygen are adsorbed, which results in their increased concentration on the carbon surface. This enhances biological

ORGANIC CONCENTRATION (COD)



CUMULATIVE WASTEWATER THROUGHPUT VOLUME

CA = TARGET EFFLUENT ORGANIC CONCENTRATION

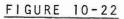
C<sub>B</sub> = MINIMUM ACHIEVABLE EFFLUENT CONCENTRATION (INDICATES "LEAKAGE" OF ORGANIC COMPOUNDS WHICH ARE ESSENTIALLY NON-ADSORBABLE, OR WEAKLY ADSORBED)

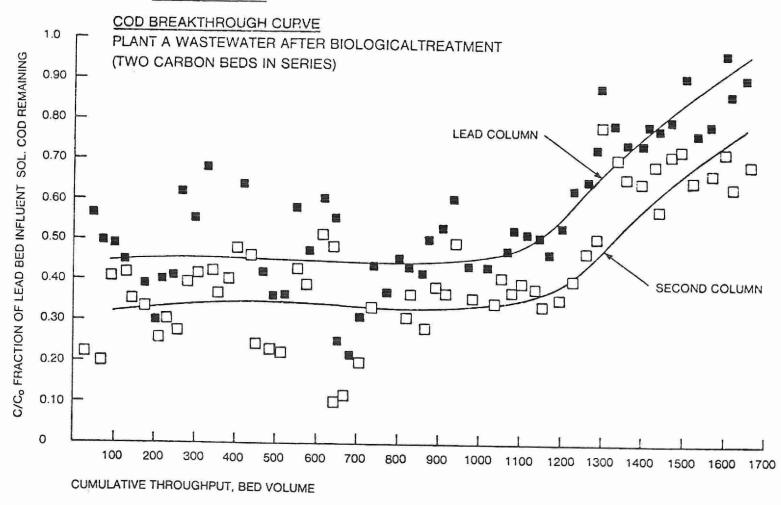
V<sub>1</sub> = CUMULATIVE WASTEWATER THROUGHPUT AT BREAKTHROUGH OF COLUMN 1

V<sub>2</sub> = CUMULATIVE WASTEWATER THROUGHPUT AT BREAKTHROUGH OF COLUMN 2

FIGURE 10-21

IDEAL BREAKTHROUGH CURVE FOR ACTIVATED CARBON





BASED ON VOLUME OF ONE BED = 5.7 LITERS/BV



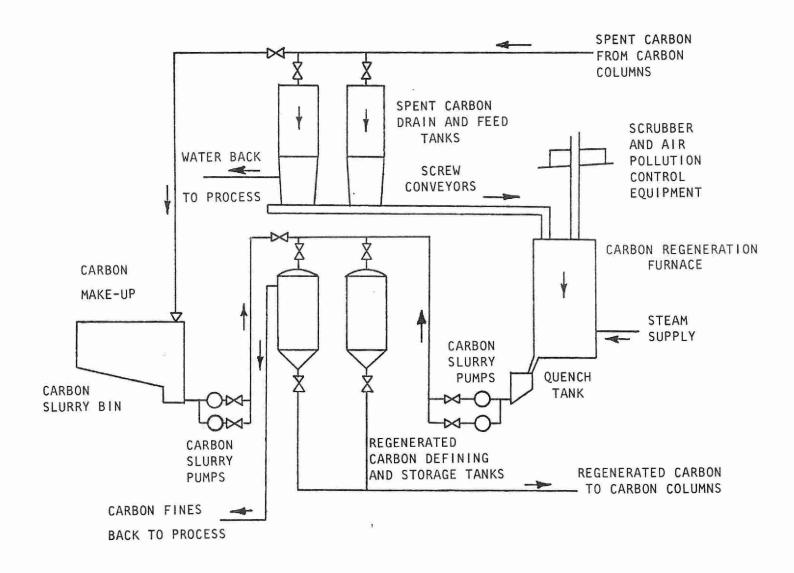


FIGURE 10-23. SCHEMATIC OF CARBON REGENERATION SYSTEM

oxidation and degradation of organics which may require a longer contact time with the biomass. Effluent COD, BOD and TOC are usually lower than without carbon addition. High density powdered carbon improves solids settling and prevents foaming. The sludge is thicker and more easily dried.

In an activated sludge containing 1000-2000 mg/l of biological solids, carbon is added to the effluent at a concentration of less than 100 g/l. The carbon is then recirculated and purged along with the sludge. The Zimpro Co. Inc. feels that the "biophysical" treatment of the effluent from a wet air oxidation process has great applicability to the treatment of toxic industrial wastes where the toxic refractory substances have survived wet air oxidation treatment and might be either toxic to the conventional activated sludge or are very slowly biodegradable (85). This process differs little from a conventional activated sludge process, except that the powdered activated carbon concentration in the aeration basin is in excess of 10,000-20,000 mg/l at the same time as the active biomass concentration is 10,000-15,000 mg/l of suspended solids. These high concentrations allow smaller aeration basins, longer sludge life, lower sludge production and rapid settling. Carbon also greatly reduces odor from the aeration basin when treating waste with volatile odorous organics. Figure 10-24 shows the flow diagram of a biophysical treatment process.

## Placement of Carbon Adsorption within Water Treatment

The efficiency of activated carbon (AC) adsorption and its placement





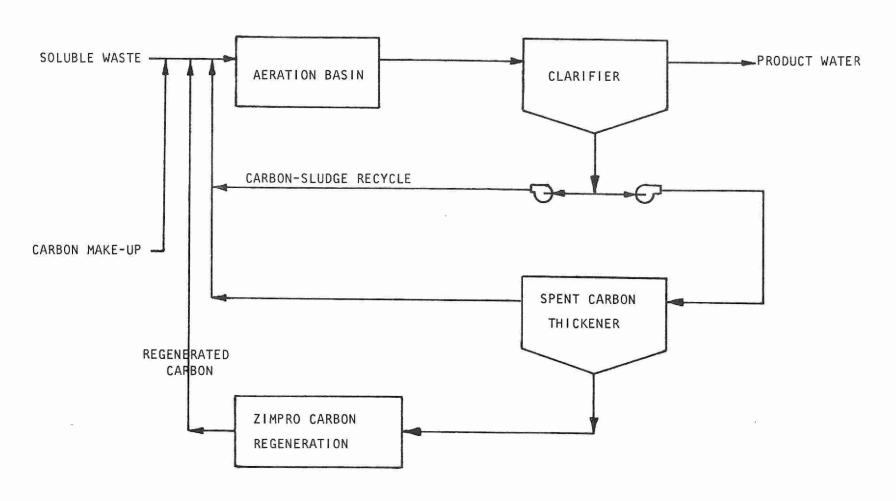


FIGURE 10-24. FLOW DIAGRAM OF BIOPHYSICAL TREATMENT

at any point in a treatment process can be determined only after a thorough investigation. Granular activated carbon adsorption - filtration can be placed prior to, or after, biological treatment, or as a total treatment process (Figure 10-25, Ford, 1972 (76)).

Biological oxidation treatment followed by AC adsorption seems to be the most attractive control process for the near future. AC adsorption works as a polishing tertiary treatment where the effluent from secondary bio-oxidation treatment does not meet the effluent quality criteria or for where refractory, hazardous and toxic organics are not removed by the secondary treatment stage.

Activated carbon adsorption could be placed prior to bio-oxidation treatment to remove biotoxic organics or for removal of occasionally high concentrations of organics which could upset the bio-oxidation treatment. Although this system has the apparent advantage of a more effective use of carbon adsorption, the final effluent has all the disadvantages of secondary biological treatment: high solids, color, less effective bio-oxidation.

Application of activated carbon adsorption as a secondary treatment is possible only in special cases. It can be used for the removal of non-bio-oxidizable or very slowly oxidizable organics, but not for TOC removal. However, the criterion is that these organics be highly adsorbable on carbon. "Leakage" of low concentration of other organics can be expected.

An economical use of AC adsorption can also be in the upstream removal of a high concentration of a single contaminant. This can be particularly useful in the case of relatively highly soluble, but still





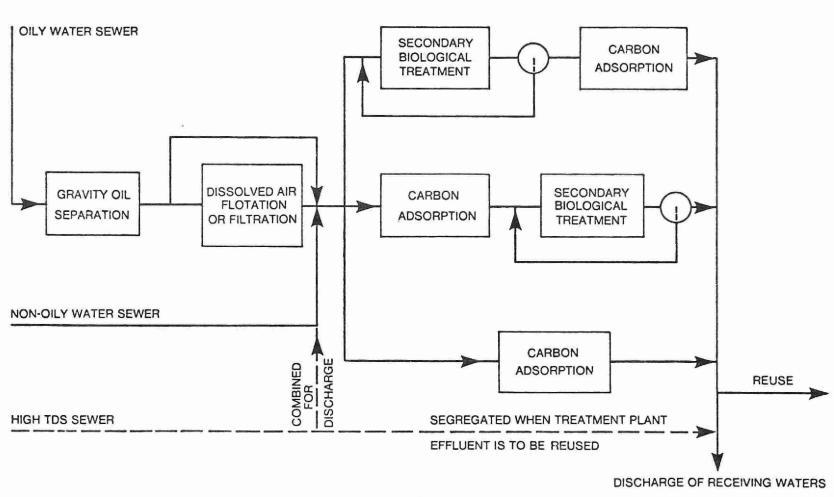


FIGURE 10-25

CANDID ITE SYSTEM APPLICATION FOR CARBON COLUMNS WITHIN A REFINERY TREATMENT COMPLEX

highly adsorbable compounds, such as benzene.

The use of powdered AC is limited today to its addition into activated sludge treatment. Though it does not produce as good an effluent quality as from biological treatment followed by AC adsorption, it may improve removal of organics, reduce solids in the effluent, improve sludge settling, and remove some refractory organics such as detergents, dyes, etc.

## 10.3.4.2.3 OTHER TREATMENT METHODS

## Chemical Oxidation

Various oxidants have been used for the oxidation of nonbiodegradable organics. Disinfection with <u>chlorine</u> is the approved practise for treating municipal drinking water supplies. However, recently, chlorinated organics have been detected in drinking water from such treatment plants and has lead to the search for a suitable alternative to chlorination.

Ozone is a stronger oxidant than chlorine. It seems to be quite effective in oxidizing high-molecular weight organics that are otherwise difficult to treat. Typical 03 reaction products are carbonyls, glycols, and acids, along with products of aromatic benzene ring cleavage. The organic oxidation products are largely biodegradable. Ozone with UV treatment reduces the concentration of various pesticides to near zero (86) and works effectively on chlorinated hydrocarbons such as pentachlorophenol, dichlorobutane, dichlorobenzene and chloroform.

Calcium Hypochlorite may be more suitable as a water disinfectant than chlorine. There is an indication that hypochlorite does not produce

haloforms such as chloroform in treated waters. Also, this chemical functions as an algicide in cooling water systems.

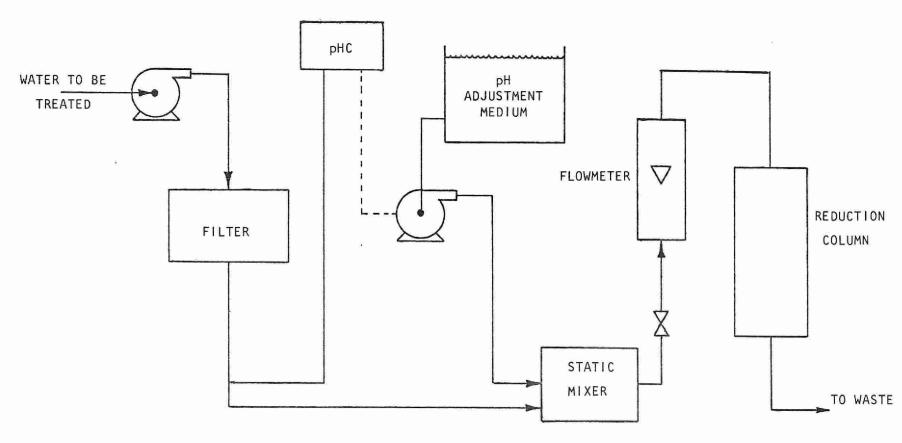
# Polymeric Adsorbents

A new separation technique has been developed by the Rohm and Haas Company using new macroretricular polymeric adsorbents that are used specifically for adsorbing aromatic and aliphatic compounds from water. Nonionic compounds such as benzene or naphthalene are reported to be removed with 100 % efficiency, Simpons, 1972 (82).

Another polymeric adsorbent was discovered by Union Carbide researchers. The adsorbent is a highly stable molecular sieve material, a polymorph of silica (SiO<sub>2</sub>) called silicalite (91). Besides its adsorbent ability, the surface of this material preferentially adsorbs nonpolar organic molecules and repels water molecules. It can adsorb any molecule the size of benzene and smaller. The material seems to be remarkably stable to very high temperatures (up to 1100 °C), which would be very useful for regeneration.

# Catalytic Reduction

A catalyzed-iron reducing agent has been reported to successfully reduce small amounts of chlorinated hydrocarbons (87). The reduction column contains catalyzed iron powder reductant (100-200 mesh) in a sand-bed matrix. Figure 10-26 shows the flow chart of the treatment. Pretreatments such as filtration for oil and solids removal, pH adjustment, etc. should be used. Reduction of chlorinated pesticides from 100 ppb-1 ppm to 1-10 ppb, and of polychlorinated biphenyl (PCB) from 200 ppb to less than 1 ppb was obtained in a field test. The





indications are that the system can also remove "light ends" such as chloroform, carbon tetrachloride and ethylene dichloride.

## 10.4 WASTE DISPOSAL METHODS

For the purpose of this report "waste" is defined as a solid or concentrated liquid material which cannot be further processed for recovery of valuable components and has to be disposed of by means of destruction to harmless compounds or stored in such a way that it is prevented from entering the environment.

Deep wells and land fills have often been used in the past to dispose of chemical wastes. However, it has become more and more difficult to find sites for disposal where there is no risk of ground water contamination. In some countries, burial of oily wastes has already been banned and it is virtually certain that such disposal will be severely restricted in most countries in the future (92).

With the latest processing technology, the production of waste in petrochemical plants is minimized. However, for this very reason, information on quantities of wastes produced and operationing parameters is not available. Incineration is considered an ultimate disposal method for refinery and petrochemical wastes.

## 10.4.1 INCINERATION

Incineration is one method used for the destruction of wastes containing liquid and solid organic compounds. The principal products of combustion of organic materials are carbon dioxide, water and ash.

Depending on the composition of the wastes and the combustion conditions, some other compounds, such as oxides of sulphur, oxides of nitrogen and halogens, may be present in the flue gas. When the combustion

products from an incineration process contain these undesirable compounds, a secondary treatment such as scrubbing and/or absorption or filtration is required to lower the concentrations to acceptable levels prior to atmospheric release. R.S. Ottinger et al (1973), (90), lists waste organic streams which may be successfully disposed of by controlled incineration. Among many other compounds, the following ones are included:

B	e	n	7	P	n	0
$\boldsymbol{\nu}$	-		-	-		-

Methyl chloride

Benzyl Chloride

Methylene chloride

Carbon Tetrachloride

Naphthalene

Chlorobenzene

Perchloroethylene

Chloroform

Styrene

Dichlorobenzene

Tetrachloroethane

Cumene

Toluene

Ethylbenzene

Trichlorobenzene

Ethlychloride

Trichloroethane

Ethylene dichloride

Xylene

Wastes may be classified into two types from a combustion point of view (94):

- combustible liquids
- non-combustible liquids

The first category contains materials having sufficient calorific

value to support combustion. The second category includes materials that do not support combustion (for example water) without the addition of auxiliary fuel.

The wastes should generally have a minimum calorific value of 16.7 to 20.9 MJ/kg to successfully support combustion in air without the assistance of an auxiliary fuel (93). Some authors consider 10.5 to 12.5 MJ/kg as the minimum for properly designed incinerators (38, 43, 98).

As mentioned in Section 10.2.1.4, there are three important parameters which influence complete incineration:

- temperature
- time
- turbulence

Only the temperature may be readily controlled after the incineration unit is constructed. This can be done by varying the air/fuel ratio. A design range of 980 °C to 1090 °C is usually desirable (90, 93). In general, materials with a low flammability limit, low flash point, and low ignition and autoignition temperatures may be combusted at lower temperatures. The lower temperature limit for direct flame combustion for such compounds is 650 to 760 °C. Once the incineration temperature is determined, the physico-chemical properties of the waste, the residence time and turbulent mixing conditions are considered when an incinerator is selected and designed.

There are a number of different types of incinerators in use (92, 94-98):



- Rotary Kiln Is a slowly rotating cylinder mounted at a slight incline to the horizontal; it is applicable to most organic wastes and well suited for solids and sludges: liquids are fired through auxiliary nozzles; a temperature between 810 °C to 1650 °C is used; residence times are from several seconds to several hours (liquids shorter, solids longer).
- Fluidized-Bed The wastes are injected into a hot agitated bed of inert granular particles, usually sand (1-3 mm diameter); it is suitable for most organic wastes; combustion temperatures up to 870 °C are used; residence times are of the order of seconds for gases and liquids and minutes to hours for solids.
- Vortex Incinerator a high velocity stream jet is supplied tangentially to the waste stream which is injected radially; an air jet atomizes the liquid feed and causes a spiral-flame effect; temperatures up to 1000 °C are used; residence times are from a fraction of a second to one second; the unit is suitable for liquid and dilute sludges.
- Cyclone Incinerator As in the Vortex Incinerator, the air and burning gases follow spiral paths; air is introduced at many points around the circumference of the hearth through inclined tangential high-velocity ports; the unit has similar applications and operating parameters to the Vortex Incinerator.

Sulfonated tars from benzene plants can be successfully incinerated in a fluidized bed incinerator (93). The vortex incinerator is used for disposal of chlorinated hydrocarbon wastes from the manufacture of chlorinated organics (93); unfortunately, no process data are available. A variety of organic chlorides, from aliphatics to PCBs, were successfully destructed in a cement kiln (100) at temperatures of 2500 °C and a residence time of up to 20 seconds. Styrene still residues can be mixed into fuel oil and used in heating furnaces (93). Dichlorobenzene, carbon tetrachloride, chlorobenzene, chloroform, ethyl chloride, ethylene dichloride, tetrachloroethane, perchloroethylene, trichlorobenzene, trichloroethane and trichloroethylene are compounds which should be mixed with another fuel prior to injection into the incinerator. Incomplete combustion may cause formation of phosgene (93).

#### Secondary Abatement

Many organic wastes cannot be incinerated without some secondary form of treatment. The inorganic content of organic sludges requires the use of a particulate matter removal system. Chlorinated hydrocarbons may produce hydrogen chloride, resulting in emissions of this compound. If there is not sufficient hydrogen in the waste material to accomplish complete conversion of chlorine to hydrogen chloride, chlorine will also be emitted. The hydrogen to hydrogen chloride, chlorine will serubbing with water, but the atmosphere.

In the absence of an adequate supply of hydrogen, trichloroethylene

is incinerated in accordance with the following reaction:

 $^{\text{C}}_{2}^{\text{HCl}}_{3}$  +  $^{20}_{2}$   $\rightarrow$   $^{2\text{CO}}_{2}$  + HCl + Cl  $_{2}$ By the addition of natural gas, all of the chlorine is converted to hydrogen chloride:

 ${\rm C_2HCl_3}$  +  ${\rm 1/2~O_2+CH_4} \rightarrow {\rm 3CO_2+3HCl+H_2O}$  In this particular case, natural gas or another auxiliary fuel would be required for complete incineration, because of the low calorific value of trichloroethylene. Usually chlorinated hydrocarbons with less than 60 to 70 % of chlorine support combustion. Hydrogen chloride in the combustion products is neutralized or recovered. Depending on the chlorine content of the incinerated waste material, 15 to 20 % hydrochloric acid can be produced (99). It can be further up-graded to the desired concentration by an extractive distillation process (38, 99). The hydrogen chloride recovery process efficiency exceeds 95 %. J.C. Zimmer and R. Guaitella (38) report tail gas concentrations of hydrogen chloride plus chlorine of no more than 10 ppm.

# 10.4.2 OTHER METHODS

Other disposal methods include (93):

- dispersal into streams
- lagooning
- deep wells
- land fills

These methods have been used in the past, but are presently considered as being environmentally unsafe for the disposal of

potentially hazardous materials.

Process modification is considered the best method to minimize undesirable emissions, effluent or discharges.

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11 SAMPLING AND ANALYSIS

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## 11.1 SUMMARY

The available literature on the sampling and analysis of selected chlorinated hydrocarbons in occupational atmospheres, food and food processing, ambient air, and water has been reviewed and critically evaluated.

Since all of the chlorinated hydrocarbons of interest here behave similarly as pollutants, the general approach of this discussion has been to consider these compounds as a class. All of the techniques described have been applied or can be applied to the sampling and analysis of these chlorinated hydrocarbons individually or in admixture. The sampling technique of choice for all of the chlorinated hydrocarbons of interest is adsorption onto activated charcoal or Tenax GC. The analysis technique of choice is gas chromatography, either used alone for individual compounds or simple mixtures containing these chlorinated hydrocarbons, or used in combination with mass spectrometer, preferably with a dedicated computer, for complex mixtures containing these chlorinated hydrocarbons.

Current research efforts in the fields of air and water pollutant analysis, using gas chromatography, point to the need for using glass support-coated capillary columns as this type of column has the resolving power required to separate complex pollutant mixtures into discrete components, for subsequent identification and quantitation.

# 11.2 INTRODUCTION

Chlorinated hydrocarbons can be found as pollutants or contaminants in occupational atmospheres, in food and food processes, in ambient air, and in both drinking water and effluent waters.

In the sampling and analysis of any given class of organic compounds, there are two approaches which may be used. The first approach is to sample and analyse a particular environment for members of a class of compounds, such as the chlorinated hydrocarbons of interest here, either individually or in simple admixture. The second approach is to sample and analyse a particular environment for all organic pollutants present, including the compounds of interest.

This second approach is the preferred strategy as, although only certain chlorinated hydrocarbons are of interest here, other organic pollutants may also be of concern, either currently or in the future, and there is also the possibility that the detection of certain other pollutants with the chlorinated hydrocarbons of interest may give indications of the source of pollution of a particular environment.

This total pollutant approach necessitates the use of a sampling and analysis technique of very great sensitivity, selectivity and resolution. All of the available sampling and analysis techniques reviewed here are discussed in light of this requirement.

There may appear to be a contradiction in the techniques described to introduce samples to a gas chromatograph, between occupational air samples and ambient air samples. Solvent description followed by solution

injection is recommended for introducing occupational air samples to a gas chromatograph, whereas thermal desorption of the whole sample is recommended for ambient air samples. The difference is due to the relative concentrations of pollutants found in each environment.

Occupational air pollutants are normally present at the ppm level, and thus, the loss in sensitivity due to using solution injection does not lower sample concentration below the gas chromatograph detection limit, and is offset by the advantages of replicate injections and compound stability using this method. However, ambient air pollutants are often present at the sub-ppb level, and the dilution factor (often 100 times) using solvent desorption and aliquot injection, may be sufficient to reduce pollutant concentrations below the lower detection limits of the gas chromatographic system. Thus thermal desorption of the whole sample to the gas chromatograph is recommended.

# 11.3 SAMPLING AND ANALYSIS OF CHLORINATED HYDROCARBONS IN OCCUPATIONAL ATMOSPHERES

# 11.3.1 INTRODUCTION

Chlorinated hydrocarbons are present in occupational atmospheres principally from their use as dry-cleaning agents, metal degreasers, paint strippers, and solvents. Industrial processes involving chlorinated hydrocarbons, in addition to their primary manufacture, are the dehydrochlorination of 1,2-dichloroethane (ethylene dichloride) to form vinyl chloride monomer, and the conversion of chlorinated hydrocarbons, principally carbon tetrachloride and chloroform, to fluorochloromethanes and ethanes. Smaller amounts of chlorinated hydrocarbons are used in pharmaceuticals manufacture, in food extraction processes, and in grain fumigant formulations.

Methods of air sampling for chlorinated hydrocarbons have included the use of evacuated gas sampling flasks (1), plastic bags (2, 3), by absorption into impingers containing meta-xylene (4), amyl acetate (5), and pyridine (6), and by adsorption onto silica gel (7-11), porous polymer beads (12) and activated charcoal (13-16).

Methods of analysis have included those based on chemical reactions such as alkaline hydrolysis (17, 18) followed by determination of released chloride ion (19-22), formation of highly colored glutaconaldehydes by the Fujiwara reaction (6, 23, 24), and estimation by the use of direct reading colorimetric indicator tubes (25-29).

Other methods based on physicochemical principles include infrared

spectrophotometry (30), direct reading halide meters (31) and gas chromatography (GC) (4, 7, 11-16, 32-35).

The most widely accepted method in North America at the present time is sampling by adsorption on activated charcoal, followed by desorption with carbon disulfide and analysis by gas chromatography (16).

### 11.3.2 SAMPLING TECHNIQUES

### 11.3.2.1 ABSORPTION INTO LIQUIDS

Liquids have been used to collect chlorinated hydrocarbons from contaminated atmospheres. Elkins et al used amyl acetate in a sampling train to collect chlorinated hydrocarbon vapors in air (5). Midget impingers containing meta-xylene have also been used for collection in conjunction with gas chromatographic analysis (4). Impingers containing pyridine solution have been used for collection in conjunction with colorimetric analysis (6).

These methods are inconvenient for sampling in industrial situations, particularly in sampling the breathing zone, and especially if several impingers in series or cooling is required for adequate collection efficiency with minimum solvent evaporation. Impingers and bubblers also present hazards from possible glassware breakage, and the collection solvents (eg pyridine) are often as much of a health hazard as the chlorinated hydrocarbons being sampled.

### 11.3.2.2 SAMPLING WITH CONTAINERS

Evacuated glass sampling flasks and plastic bags have been used to sample chlorinated hydrocarbon vapors (1-3). The use of these devices may result in sample loss due to adsorption on the walls, or to

permeation through the wall of a plastic bag. Also these devices are inconvenient to transport to and from the laboratory.

## 11.3.2.3 SAMPLING BY ADSORPTION ONTO POROUS SOLIDS

Williams and Umstead (12) have reported the use of porous polymer beads as a collection medium for chlorinated hydrocarbons. With this sampling method, the same column was used for sample collection and GC analysis. This method has the disadvantage that only one analysis could be made for each sample.

Silica gel has been used to sample industrial atmospheres for chlorinated hydrocarbons (7-11). However, silica gel is a polar adsorbent and shows pronounced selectivity towards polar compounds, particularly water, in preference to less polar or non-polar molecules such as chlorinated hydrocarbons. A study by Cropper and Kaminski (11) indicated that water vapor in an industrial atmosphere could displace chlorinated hydrocarbon vapors when sampling more than 3 l of air through a 2.5 cm silica gel collection tube. Feldstein et al (10) found the same problem of low retention of chlorinated hydrocarbons on silica gel in the presence of large amounts of water vapor. Whitman and Johnston (36) used molecular sieve 5A as a prefilter to remove water vapor in a study of aromatic hydrocarbon sampling by silica gel. However, a problem with the use of molecular sieves for this purpose is the possibility of retention of compounds of interest on the filter.

Otterson and Guy (13) showed that by using carbon disulfide as a desorbing solvent, activated charcoal could be used to collect atmospheric

vapors for analysis by GC. White et al (14), at the U.S. National Institute for Occupational Safety and Health (NIOSH), chose the charcoal adsorption technique of Otterson and Guy after conducting a literature survey of available sampling and analysis methods for solvent vapors in air. They systematically evaluated collection efficiency, carbon disulfide desorption efficiency, and quantitative determination of 14 solvents using activated charcoal sampling and GC analysis. The sampling and analysis techniques developed by these workers were accepted by the Occupational Safety and Health Administration (OSHA) as standard methods for compliance investigations (16, 37). Trapping efficiencies of the activated charcoal for chlorinated hydrocarbons were reported to be in the 85-100 % range.

Because of the low polarity of an activated charcoal surface, organic materials are adsorbed preferentially to water and thus adsorption of water is not as great a problem using charcoal as it is where silica gel is used.

The use of activated charcoal tubes to sample occupational atmospheres is now an accepted method in North America, and provides adequate sensitivity for the monitoring of chlorinated hydrocarbons. However, certain limitations must be considered in the collection of solvent vapors with charcoal tubes:

- (a) Charcoal tubes have saturation limits for each compound vapor sampled. When this limit is exceeded, breakthrough occurs.
- (b) Vapors collected can be displaced by other vapors which are more strongly adsorbed by the charcoal.

- (c) High humidity affects the breakthrough volume of the charcoal. Breakthrough efficiency must be determined for expected conditions under which sampling will be carried out.
- (d) Activated charcoal is very prone to artifact formation.
  The batch of charcoal used to prepare sampling tubes should be evaluated for artifact formation from the compounds of interest.

### 11.3.3 ANALYSIS TECHNIQUES

Analytical methods for determining chlorinated hydrocarbons collected from industrial atmospheres can be divided into two broad categories: methods based on chemical reactions of the chlorinated hydrocarbons and methods based on their physicochemical characteristics.

### 11.3.3.1 CHEMICAL ANALYSIS TECHNIQUES

Three chemical methods have been used extensively to determine chlorinated hydrocarbons. These are dechlorination of collected vapor samples with strong bases (17, 18) followed by titration of the chloride ion (19-22), colorimetric measurement of the reaction products of chlorinated hydrocarbons and pyridine heated in alkaline solution (Fujiwara reaction) (6, 23, 24) and direct reading colorimetric indicator tubes (25-29).

The dechlorination method (alkaline hydrolysis) requires collection of the chlorinated hydrocarbons by a suitable collection method followed

by hydrolysis in isopropyl alcohol. Solid potassium hydroxide is added to the reaction mixture, and this mixture is allowed to stand overnight (20 hours). After neutralization the liberated chloride ion is determined. The chloride ion may be estimated by titration using the Volhard method (18), the Mohr method (38), or with adsorption indicators (20, 21). Each of these methods involve direct or indirect titration of the liberated chloride with silver nitrate. The chloride ion has also been measured by potentiometric methods (22).

Two disadvantages of the alkaline hydrolysis method are that the dechlorination step is dependent upon the degree of hydrolysis, and the method is not specific for any individual chlorinated hydrocarbon in the presence of other chlorinated hydrocarbons.

In the colorimetric analytical method based on the Fujiwara reaction, a stream of air containing the chlorinated hydrocarbons of interest is passed through a wash bottle containing pyridine. Methylethylketone (MEK) and sodium hydroxide (NaOH) are then added to an aliquot of the sample pyridine solution and this mixture, together with a blank aliquot of the MEK/NaOH solution, is heated in a boiling water bath and cooled for a specified time period. The chlorinated hydrocarbons form glutaconaldehydes of characteristic color, and the absorption coefficient of this solution at an optimum wavelength is determined with a spectrophotometer, along with the absorption coefficient of the blank solution. This method is not specific when mixed chlorinated hydrocarbons are present, and the color intensity produced depends on the degree of chlorination of the hydrocarbons, with chloroform and 1,1,1-trichloroethane producing the highest color intensity (39).

A third chemical method utilizes direct reading detector tubes.

Glass tubes are packed with chemicals impregnated on solids (usually silica gel) that change color when a metered and controlled flow of air containing chlorinated hydrocarbon vapors is passed through the packed material. The test vapor may be drawn directly through the tube and compared with a calibration chart, or it may be drawn into a pyrolyzer and then through the packed tube (25). Several reagents are used in these tubes, depending upon the particular chlorinated hydrocarbon for which the tube is designed. Some of these reagents are more specific for a particular chlorinated hydrocarbon than others, but the methods generally depend on estimating the length of a colored zone produced by a reaction of liberated chloride ion, and in these cases the presence of chlorine or other chlorinated hydrocarbons cause interferences. The tubes are not sensitive enough for those chlorinated hydrocarbons with very low Threshold Limit Values.

### 11.3.3.2 PHYSICOCHEMICAL ANALYSIS TECHNIQUES

The analytical methods based on physicochemical properties of chlorinated hydrocarbons include those using infra-red (IR) spectrophotometry (30), photochemical analyzers (halide meters) (31), and gas chromatography (4, 7, 11-16, 32-35).

Barretta et al (30) have described a method which uses an IR analyzer to continuously monitor industrial atmospheres for chlorinated hydrocarbons. With this method, concentrations are measured directly, and it is not necessary to collect individual samples for transportation to a laboratory

for analysis. However, this method has several disadvantages. The necessary instrumentation for continuously sampling the atmosphere and recording concentration data is complex. It is also important that the atmosphere of relevant working stations within a plant is sampled and that such samples correspond to the breathing zones of the workers at these stations. This is difficult to achieve with automated instrumentation. A further disadvantage is that IR spectrophotometry is subject to interferences from other air constituents, and cannot easily distinguish between chlorinated hydrocarbons in admixture.

Halide meters detect the increased brightness of an AC arc (metal electrode) when it is enveloped by an atmosphere contaminated with halogenated hydrocarbons (31). These instruments are sensitive to all halogens and halogenated compounds, and consequently are not specific for a given chlorinated hydrocarbon.

Of the various methods of analysis, gas chromatography offers the greatest specificity and sensitivity. The flame ionization detector (FID) is sensitive enough to detect chlorinated hydrocarbons down to the ppm level. For detection of smaller amounts than this, an electron-capture detector (ECD) may be used, but ECD sensitivity is highly dependent on the degree of chlorination of a particular hydrocarbon (polychlorinated hydrocarbons being most sensitive), and the ECD, particularly on older instruments (which may still be in use), is affected by oxygen, which causes anomalous responses by removing part of the electron current of the detector by a charge-transfer process.

A literature survey carried out by White et al (14) in 1970 found that the GC was most often mentioned as the analytical tool of choice for the determination of organic vapors in industrial atmospheres. They also described a method of sampling for 14 solvents by charcoal adsorption, desorption with carbon disulfide, and analysis by GC. This method is currently used by NIOSH in compliance investigations (16).

A disadvantage of this method is in the use of carbon disulfide as the desorbing solvent. This solvent, even when of the highest purity available, may contain trace amounts of impurities whose retention times overlap those of the chlorinated hydrocarbons. This overlap can cause identification difficulties and limit detectability.

The most widely accepted GC column material for chlorinated hydrocarbon analysis is a 10 % Carbowax 20M terephthalic acid derivative (commonly called FFAP) on acid-washed, silanized 80/100 mesh Chromosorb W. It should be noted that several stationary phases and supports of similar composition are available from different proprietary suppliers. A 10 or 20 ft. x 1/8 in. stainless steel column is generally used. A 10 ft. column is used for the lower boiling point chlorinated hydrocarbons, and a 20 ft. for the higher boiling point compounds (16).

The most reliable and reproducible method of introducing samples to the GC is via syringe injection using the solvent flush technique.

Mass spectrometry (MS) can also be used with GC to identify more positively the chlorinated hydrocarbons present. Cooper et al (33) have described the use of a capillary charcoal tube to trap the compounds

individually as they elute from the GC for transfer to the MS inlet system and subsequent identification. Combined GC-MS instruments are also available.

GC is the preferred technique for analysing chlorinated hydrocarbon vapors in industrial atmospheres because of its superior qualities of selectivity, sensitivity, ease of operation and short analysis time with minimum sample handling required.

## 11.4 SAMPLING AND ANALYSIS OF CHLORINATED HYDROCARBONS IN FOOD AND FOOD PROCESSING

### 11.4.1 INTRODUCTION

Chlorinated hydrocarbons are used in certain applications within the food processing industry. Carbon tetrachloride, 1,1-dichloroethane, chloroform and trichloroethylene are used in fumigant formulations for treatment of cereal grains. From this application, traces of these compounds appear in bread and cereal products, and it is possible that these compounds and their metabolites may be present in meat and meat by-products for human consumption through the use of fumigated grains as animal feed.

Methylene chloride, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene are used as solvents to extract certain consitutents of foods. For example, methylene chloride is used to extract flavor constituents from beer hops, and trichloroethylene is used to extract caffeine from coffee beans for use in the production of decaffeinated coffees. Potential applications of chlorinated hydrocarbons in this field include the extraction of oil from seeds, vapor peeling of fruits (particularly tomatoes), dewaxing of fruits, the solvent-promoted dehydration of foods (particularly fish protein concentrates), and in the treatment of waste waters from food processing to lower BOD levels (40).

Considerable effort has been devoted to the sampling and analysis of chlorinated hydrocarbon residues from the fumigation of grains and cereals. However, methods used in this field are readily applicable to analysis of chlorinated hydrocarbon residues in other food products.



### 11.4.2 SAMPLING TECHNIQUES

Sampling of chlorinated hydrocarbons used in fumigants usually relies on three techniques. Grab samples during and after fumigation are taken with glass containers (41) for subsequent GC analysis. Chlorinated hydrocarbons adsorbed onto the grain surface can be sampled by cold extraction with acetone or acetone/water (41, 42) or by steam distillation into a suitable solvent, eg toluene (42). However, Scudamore and Heuser (42) found that steam distillation recovered only about 70 % of the chlorinated hydrocarbon residues (carbon tetrachloride in this study) detected by the cold extraction method. They also found that some of the carbon tetrachloride was converted to chloroform.

Cold solvent extraction appears to be the best sampling method for chlorinated hydrocarbons present in grain as fumigant residues. However, complete extraction of compounds that are strongly chemisorbed to the grain surface may not be realised (42).

### 11.4.3 ANALYSIS TECHNIQUES

The most widely used analysis technique for fumigant residues is GC.

A variety of GC detectors are available but the most common ones used are FID, ECD, and thermal conductivity (TCD).

ECD, although the most sensitive detector for most of the chlorinated hydrocarbons, does not exhibit the same low limits of detectability to all chlorinated hydrocarbons. For example, chlorobenzene gives a very poor response with ECD, 1,2-dichloroethane has a limit of detectability of 1.5 ng, while carbon tetrachloride has a lower limit of 5 pg. These

differences in detection limits should be considered in analyses of chlorinated hydrocarbon residues in admixture.

An excellent review of the methods of analysis for fumigants and fumigant residues has been given by Berck (43). Earlier reviews in the field are cited. A number of other analysis techniques including polarography, selective ion electrodes, and spectrometry are also discussed.

## 11.5 SAMPLING AND ANALYSIS OF CHLORINATED HYDROCARBONS AS AMBIENT AIR POLLUTANTS

### 11.5.1 INTRODUCTION

In typical ambient atmospheres, vapor-phase organic pollutants are generally present at very low concentrations. The proper evaluation of these organic pollutants depends directly on their collection and transport to the laboratory with a minimum of sample loss or reaction.

Because of the very broad range of organic chemical species present in polluted air, and the possibility of reactions or irreversible adsorption, they present many difficult sampling problems.

Many different methods of sampling polluted air have been described. Direct methods of collection include the use of glass bottles (44), plastic bags (45), and stainless steel containers (46).

Indirect enrichment methods include condensation and absorption with or without chemical reaction (47) and adsorption on various solids (48-52).

The analytical technique of choice which gives the required specificity and selectivity for chlorinated hydrocarbon pollutants is gas chromatography. Identification of these components in complex mixtures requires the use of a GC/MS system, preferably with a dedicated computer and appropriate software for data reduction and manipulation.

### 11.5.2 SAMPLING TECHNIQUES

#### 11.5.2.1 GRAB SAMPLERS

A technique commonly used in air pollution investigations is "grab" sampling. The procedure is to rapidly acquire a volume of air that can

later be analysed for specific pollutants. The containers are normally plastic bags, glass flasks or syringes, or metal cylinders.

Ohta et al (53) used 10 cm<sup>3</sup> glass syringes to sample ambient air for chlorinated hydrocarbons in a study in Tokyo in 1974-75. 10 cm<sup>3</sup> air samples were taken and analysed within 20 hours by GC/ECD. Four chlorinated hydrocarbons (carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene) were monitored and annual average concentrations were estimated to be 0.8, 1.4, 1.2 and 1.2 ppb respectively. One problem with the method was the possibility of systematic error occurring due to air exchange with the syringe contents and ambient laboratory air during storage. Chloroform could not be analysed for this reason because chloroform levels in the laboratory air were too high. However, these workers reported the method satisfactory for the four compounds measured with analytical error being below 10 %.

Lillian et al (54) used  $100 \text{ cm}^3$  glass syringes in a study of ambient levels of eleven halocompounds in the air along part of the East coast of the U.S. The compounds monitored were fluorotrichloromethane, dichlorodifluoromethane, 1,1,1-trichloroethane, carbon tetrachloride, tetrachloroethylene, trichloroethylene, methyl iodide, sulfur hexafluoride, ethyl chloride, chloroform, and 1,1,2-trichloro-1,2,2-trifluoroethane. The halocompounds were analysed by GC/ECD and GC/FID. These workers reported less than 10 % halocarbon loss in the syringes over a 48 hour period. The standard deviation for concentrations of all compounds except  $\text{CC1}_2\text{F}_2$  was reported to be  $\frac{1}{2}$  15 %. Measured amounts were at the ppb and sub-ppb level.

The main limitation to the use of these containers is the small volume of air that can be collected. Metal containers have the advantage that air samples can be compressed up to several atmospheres, but wall adsorption effects may still be a problem, particularly during transportation and storage.

Samples collected in plastic bags must be analysed within a short time period (4 hours) due to possible losses from wall adsorption, or diffusion through the walls of the bag.

### 11.5.2.2 CRYOGENIC COLLECTION

Cryogenic methods are particularly suitable for analysis of highly volatile substances. However, if liquid nitrogen, liquid oxygen or solid carbon dioxide/acetone is used as a coolant, large quantities of water may accumulate. This can cause a major problem during subsequent GC analysis (52). Drying the air sample by passing it over dessicants prior to cryogenic trapping is not feasible since some compounds of interest may also be removed (55, 56). Aerosol formation may also occur with this technique reducing trapping efficiency.

Simple open-bore, cryogenic traps are now seldom used in air pollution studies (57).

#### 11.5.2.3 ABSORPTION TECHNIQUES

Morita and Ohi (58) used the hexane impinger technique of Miles et al (59) to sample paradichlorobenzene in Tokyo air and in an indoor environment. An ice/salt bath was used to minimize solvent evaporation. The samples were analysed by GC/ECD. Reported levels of para-dichlorobenzene were 1.5-4.2 ng/m<sup>3</sup> in outdoor air, and 105-1700 ng/m<sup>3</sup> indoor. The high indoor level was presumably due to the use of paradichlorobenzene



as a deodorant and as a moth repellant. Levels of precision and accuracy were not reported.

The use of impinger systems are generally inconvenient, requiring the transport and handling of liquids in the field. The requirement of solvent cooling to minimize evaporation is also an inconvenience, particularly if several impingers in line are required for adequate collection efficiency.

### 11.5.2.4 COLLECTION BY ADSORPTION

The evaluation of adsorbents for concentrating organic vapors from ambient atmospheres should be based on the following criteria: quantitative collection efficiencies and recovery of trapped vapors, high breakthrough volumes, minimal decomposition or polymerization of sample constituents during collection and recovery, low background contribution from the sorbent, and little or no affinity by the sorbent for water (51).

The performance of many adsorbents as to their ability to extract and retain organic vapors from an air stream has not been adequately studied. The parameters involved in determining the performance of sorbents can be divided into two categories. There are those relating to the sampling environment such as flow rate, air temperature and humidity, and those related to the physicochemical properties of the sorbent such as surface area, particle size and porosity, solute capacity, sorption mechanism and degree of solute affinity. Also, some of these factors which influence sorbent performance are not independent of each other (51).

A sampling method which is based on gas chromatographic principles employs liquid phases uniformly coated on solid supports. These liquid phases exhibit solution formation with trace organic vapors in the atmosphere at ambient temperatures.

Other sorbent materials that have been described are chemically bonded stationary phases (60, 61), polymer beads (62-65), and activated carbon (66).

In 1970, Van Wijk described a new type of porous polymer (67, 68), Tenax GC. This is a polymer of 2,6-diphenyl-para-phenylene oxide which exhibits very high temperature stability. Several applications of Tenax GC have been described (48-50, 69-71).

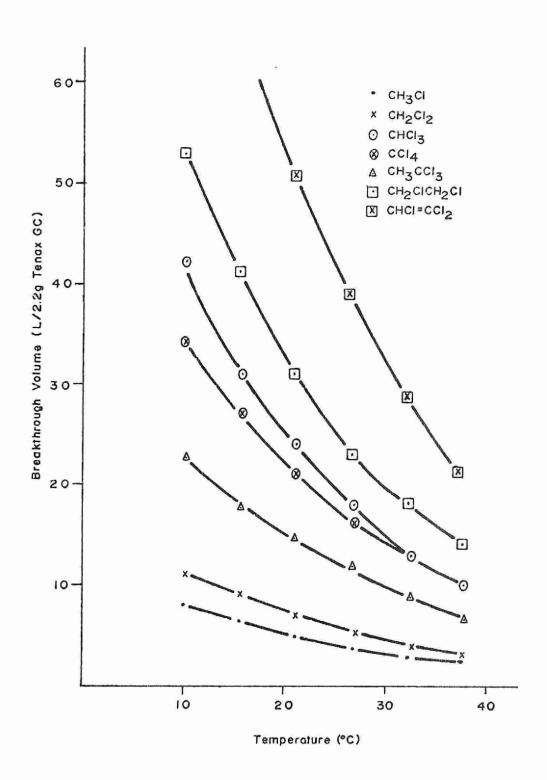
Recently, Pellizzari and co-workers have carried out an extensive characterization study of different sorbents for air sampling (51, 52, 72-77). The sorbents studied were Chromosorb 101, Chromosorb 104, Chromosorb W-HP, Carbowax 400/Porasil C (chemically bonded), oxopropionitrile/Porasil C (chemically bonded), phenylisocyanate/Porasil C (chemically bonded), Porapak Q, activated carbon, Tenax GC and the stationary phases Carbowax 600, dodecylphthalate and tricresylphosphate coated on Chromosorb W-HP. These workers found that all of these materials, except tricresylphosphate and dodecylphthalate, showed good collection efficiency for a variety of compound classes. However, on carrying out thermal desorption studies, they found that all of the sorbents except Tenax GC, Chromosorb 101, and activated carbon showed high backgrounds of organic compounds which were thermally desorbed (72).

These workers then carried out studies on these sorbents for flow characteristics, pressure differential of different particle size in a packed bed, and determination of elution and breakthrough volumes for a series of compound classes. From these and subsequent studies, it was concluded that Tenax GC was the preferred sorbent for use in air pollution studies because of its low affinity for water, high thermal stability, and high breakthrough volume for the greatest number of compounds. However, Tenax GC is generally not a good sorbent for  $c_1-c_5$  organic vapors, and some of the chlorinated hydrocarbons of interest (77, 78). Methyl chloride, methylene chloride, chloroform, carbon tetrachloride, 1,2dichloroethane and l,l,l-trichloroethane show low breakthrough volumes ranging from 5-31 litres of air aspirated through 2.2 g of Tenax GC at 21.2 °C (74). The breakthrough volumes of these compounds on Tenax GC over a range of ambient temperatures are illustrated in Figure 11-1. For these compounds activated coconut charcoal is used as a backup to Tenax GC. The significant accumulation of water on activated charcoal is a problem, which can be overcome by desorbing the compounds collected on activated charcoal onto a Tenax GC sampling cartridge with a volume of pure air sufficient to remove the water (water has a breakthrough volume of 0.04 1/2.2 g Tenax GC at 21.1 °C) (74, 77), while not exceeding the breakthrough volumes of the compounds of interest.

Tenax GC, backed up by activated charcoal, is the best sorbent currently available for air pollution studies. However, the low break-through volume exhibited for some low carbon number chlorinated hydrocarbons, and the undesirable characteristics of activated charcoal (high retention

## FIGURE 11-1

# BREAKTHROUGH VOLUMES FOR SOME CHLORINATED HYDROCARBONS ON TENAX GC OVER A RANGE OF AMBIENT TEMPERATURES



of water and high surface activity which make possible artifact formation an important consideration) show the need for the development of a complementary adsorbent to Tenax GC for sampling C<sub>1</sub>-C<sub>5</sub> organic compounds which still retains the desirable characteristics of Tenax GC (77, 78). A material recently developed by Union Carbide (79, 80) shows promise as a candidate for this complementary adsorbent. The new material is a polymorph of silica called silicalite and has a highly stable molecular sieve structure. The material is reported to be extremely hydrophobic, preferentially adsorbs non-polar organic molecules, and the void spaces within its structure are wide enough to adsorb molecules up to about 0.6 nm in diameter, which include most of the smaller size chlorinated hydrocarbons of interest here. Further investigations are needed to characterize this material for this application.

### 11.5.2.5 DIFFUSION SAMPLERS

A novel approach to sampling for atmospheric pollutants has recently been described by French and Reid (81). This approach is based on establishing a defined diffusion gradient for specific compounds between ambient air and a collection medium impregnated with activated charcoal. The technique described by French and Reid uses a small device (passive dosimeter) whose geometry is such that organic vapors in the air diffuse through a carefully defined diffusion layer for a known period of time. After sampling is completed, the activated carbon collection element is transferred to a small vial, and the trapped organic vapors are desorbed by an appropriate solvent, normally carbon disulfide. The solution is subsequently analysed by gas chromatography.

The major advantage of using these passive dosimeters is that they are of low cost and do not require the use of mechanical pumps to draw air over the adsorbent to collect organic pollutants. However, these dosimeters are designed for sampling organic vapors at the 10-100 ppm level in occupational environments, and several difficulties arise when applying them to ambient air sampling at the ppb level (81). The dosimeter housing may be a source of contamination from compounds leaching from the plastic materials used in its construction. Also the dosimeter closure method is poor, allowing contaminants to leak into those dosimeters used for blanks. Other difficulties arise mainly from the use of activated charcoal as the adsorbent (high surface activity, batch to batch variation, irreversible adsorption of organic vapors) and from the analysis method used. Solvent desorption directly to the GC (see Section 11.5.3.1.1 below), and impurities in the solvent used can cause serious interferences in the GC analysis.

This method shows great promise as a low cost sampling method for air pollutants. However, the problems associated with the method must first be solved before these passive dosimeters can be applied to systematic air pollution studies.

### 11.5.3 ANALYSIS TECHNIQUES

### 11.5.3.1 GAS CHROMATOGRAPHY

For the analysis of organic pollutants in ambient air, the method of choice is gas chromatography. While there are still many difficulties and limitations to GC analysis, particularly detector sensitivity and

column technology, it is the best analysis technique which has the potential to offer the necessary specificity, sensitivity, versatility and speed of analysis to measure trace contaminants that constitute the complex mixture of organic compounds present in polluted air.

### 11.5.3.1.1 SAMPLE INTRODUCTION

Many different GC analysis methods have been reported. Methods of desorption from sorbents include solvent extraction (82), and thermal desorption directly into the GC inlet (48, 49, 51, 61, 64). The use of solvent extraction alleviates problems of artifact formation associated with thermal desorption, such as pyrolysis, polymerization or incomplete recovery. However, volatile pollutants cannot be quantitatively concentrated from dilute solutions and since GC analysis is limited to small aliquots of liquid samples, only a fraction of the sample can be analysed (51, 72). As a result, overall sensitivity using a solvent extraction method is reduced.

Despite the large concentration effect for organic vapors using adsorption sampling methods, only trace quantities of these compounds are accumulated; thus it is often necessary for the entire sample to be submitted for analysis (51). Thermal desorption is the most popular method of transferring the entire amount of trapped vapors to the analytical system (48, 49, 51, 52, 56, 64, 72-78, 82, 83). The method used by Pellizzari et al (51, 52, 72-76, 83) is fairly typical, but includes some interesting design features. The apparatus consists of an aluminium heating block in which the Tenax GC sample cartridge is

sealed during desorption. The collected pollutant vapors are purged from the heated cartridge into a gold-plated nickel capillary trap held, typically, at liquid nitrogen temperatures. The trap is designed to allow a thermal gradient to develop between the top and bottom of the trap. This feature essentially eliminates aerosol formation during condensation. After the sample is condensed in the trap, it is transferred to the GC by flash heating and purging with carrier gas. As heating commences from the top of the trap, a thermal gradient is again established which acts to concentrate the sample vapors into a narrow plug as they enter the GC column (77). Small traces of water trapped during sampling do not interfere with component separation and identification.

### 11.5.3.1.2 COLUMN TECHNOLOGY

A wide variety of column types and packings are now used in the separation and identification of complex mixtures of organic compounds. These column types include conventional packed columns, open tubular capillary columns, support-coated capillary columns, and packed capillary columns. However, gas chromatographic analysis of the hydrocarbon contaminants in polluted atmospheres have, until recent years, remained almost the exclusive realm of packed columns. These columns do not all provide sufficient resolution to adequately separate the broad range of components detected in urban atmospheres or to make the highly accurate retention time measurements needed for identification purposes. Several recent applications of packed columns to GC analysis of chlorinated hydrocarbons have been reported (53, 58, 84-87).

Mayrsohn et al (88) have used temperature programming in conjunction with small diameter (0.01 in.1.D.) wall-coated open tubular (WCOT) columns to achieve high resolution of the atmospheric burden of  ${\rm C_2^{-C}_{10}}$  organic compounds on a routine basis. However, the restricted sample capacity of the 0.01 in. 1.D. capillary columns limits the sample volume for analysis, which greatly reduces the sensitivity for analysis.

Rasmussen and Holdren (89) reported using a 200 ft. 0.02 in. I.D. support-coated open tubular (SCOT) column with an OV-101 substrate operated in a sub-ambient temperature program mode for routine analysis of aliphatic organic compounds at trace (0.01 ppb) background concentrations. The SCOT column has an inherently larger sample capacity than 0.01 in.

I.D. capillary columns, is durable, and exhibits high resolution. This type of column has the advantages characteristic of both the open tubular and packed columns, without the pressure drop of packed columns or the low sample capacity of capillary WCOT columns (90). Pellizzari (52, 74-77) routinely uses glass SCOT columns with a variety of stationary phases to analyse ambient air samples.

The main technological difficulties associated with the use of glass SCOT columns is the achievement of uniform distribution of the liquid phase and support on the column wall and control and measurement of flow rate during analysis (91). However, by careful control and calibration techniques these problems can be overcome (77).

A new type of chromatographic packing material has recently been

reported (92-95). This material consists of a tightly bound, ultrathin film, less than 1.5 nm thick and approximately 0.2 weight percent, of liquid phase on a solid support (usually Chromosorb W). This material has highly desirable chromatographic properties. It exhibits short retention times, high selectivity, low bleed, and excellent peak symmetry and resolution for highly polar compounds (92). Liquid phases reported to form this film are Carbowax 20M, SE-30, AN-600, DEGS and linear polyethylene, using Chromosorb W as solid support (93, 94). A description of these new materials, including preparation and applications, has been published by Karasek and Hill (95).

### 11.5.3.1.3 GC DETECTORS

Two types of detectors are currently used to analyse ambient air for chlorinated hydrocarbons. These are the FI and EC detectors. Both types can easily detect these compounds at the ppb level, but the ECD can detect polychlorinated hydrocarbons down to the ppt level. The choice between which of these two detectors to use in a routine analysis schedule depends on the amount of information required. If the analysis of polychlorinated (3-4 Cl) hydrocarbons only is of primary interest the ECD is the detector of choice. However, this detector is no more sensitive than the FID for determining levels of methyl chloride, methylene chloride, 1,2-dichloroethane or chlorobenzene (eg ECD detection limit for 1,2-dichloroethane is 1.5 ng compared with 6 pg for carbon tetrachloride (43)). On the other hand, if the total burden of atmospheric pollutants is to be separated, characterised and quantified, the FID is a far

response to all classes of organic pollutants, including chlorinated hydrocarbons, wereas the ECD requires that an organic compound be capable of capturing electrons for its detection, and shows little or no response to organic compounds which do not easily undergo this process.

The choice of GC detector also affects other parts of the sampling and analysis process. A much smaller air sample volume is required for analysis of polychlorinated hydrocarbons with the ECD (eg 5-100 ml samples (53, 54, 84-86)). This is because the ECD performance is greatly affected by large concentrations of strongly electron-capturing compounds (eg carbon tetrachloride). Too large a concentration of such a compound saturates the ECD electron current, and a considerable time may be required for the compound to be purged from the detector and the electron current to return to normal levels.

A consequence of smaller sample volumes is that, if MS is used for compound identification, a chlorinated hydrocarbon detectable by the ECD at the pg level will give too low a response in the MS for adequate characterization (77).

Because of these and other considerations, and the amount of research effort needed to produce a reliable sampling and analysis technique, either the class analysis technique or the total component analysis technique must be chosen.

In a comprehensive air pollution characterization program, the total component analysis technique is preferred. This is because other

types of compounds may become of concern in the future, and a general analysis technique already available, of the necessary specificity and sensitivity, obviates the need for further research and development effort (77).

### 11.5.3.2 MASS SPECTROMETRY

MS coupled with appropriate auxiliary techniques (such as GC, computer-assisted data processing, and specific ion detection) has the potential to be used to advantage in determining the various relevant organic air pollutants present at the sub-nanogram level. MS has a relatively uniform high sensitivity for all chemical species that can be volatilized, excellent selectivity from interfering materials by use of specific ion detection or high resolution, and it can easily identify unexpected compounds.

High resolution mass spectroscopy (HRMS) has been used by Crittenden and co-workers (64, 96) to analyse air pollutants without GC separation. These workers were able to introduce to the mass spectrometer gaseous pollutants collected on Chromosorb 102 and desorbed by a thermal-vacuum technique. They found the technique useful for characterizing the organic fraction of polluted air. However, unambiguous identification of specific compounds was seldom possible without the use of data from other analysis techniques.

### 11.5.3.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GC-MS is presently a widely used and powerful tool for organic analysis. Interfacing of the GC-MS system with a dedicated minicomputer,



and a variety of output devices such as a CRT, teletype, or XY plotter, and a high speed line printer has become a necessity and common practice.

Mass spectra may be obtained by electron impact ionization (EI) or by chemical ionization (CI). In the latter mode, sample ionization is accomplished by means of an ionized reagent gas. In GC-CI-MS analysis, the reagent gas, such as methane or isobutane, may be introduced through its use as the GC carrier gas, with no molecular separator being used at the interface between the GC and the MS. MS ionization pressure with CI using methane, for example, is typically as high as 1-2 torr, and thus a far higher concentration of methane than sample in the MS ionization source ensures that sample ionization will occur exclusively by collision with ionized methane. CI results in a much different mass spectrum than El in view of its being a much lower energy process. Cl spectra are characterized by less extensive fragmentation of the molecular ion, and the fragmentation which occurs generally proceeds through the loss of neutral species and gives appreciably more stable fragments than is the case with El (97). usual to observe a protonated molecular ion in CI, and this is frequently accompanied by two adduct ions at M+29 and M+41 (for methane CI) caused by the addition of  ${}^{\rm C}_2{}^{\rm H}_5^{\star}$  and  ${}^{\rm C}_3{}^{\rm H}_5^{\star}$  radicals to the molecule in the MS source. Such adduct ions are generally diagnostic for the protonated molecular ion, and thus it is frequently possible to quickly assign a molecular weight during GC-CI-MS analysis.

Since CI analysis is still relatively new, EI analysis maintains a

significant advantage and is well suited to the analysis of organic compounds in complex mixtures. Over the past few years, extensive data files of EI spectra have been built up, many of these given particular emphasis to toxic and hazardous materials. Spectral matching is a very useful aid to the interpretation of unknown EI sepctra, which, when coupled with other analytical data, can frequently lead to a reasonable interpretation of the mass spectrum. However, because of the complex mixtures encountered in air pollutant analysis, some components are not completely resolved. To obtain clean spectra for matching purposes, a peak deconvolution program recently devised by Rindfleisch is reported to be a very useful aid to interpretation (77, 78). The spectral stripping technique devised by Biller and Beiman (98) has been the best deconvolution method developed, but sometimes this technique gives ambiquous results (91).

The basic routines available with all commercial mini-computers for GC-MS are RGC (reconstructed gas chromatogram), mass spectral printing, mass chromatograms and selected ion monitoring.

The normal RGC plot consists of a reconstructed chromatogram which contains ions of all mass numbers, commonly called a "total ion chromatogram". In order to locate the GC peaks for compounds of interest for which mass spectra are known, RGC plots containing prominent ions in the mass spectra of these compounds may be made. The plots are commonly called "mass chromatograms". As chlorine exists in nature as an isotopic mixture of Cl<sup>35</sup> and Cl<sup>37</sup> in a 3:1 ratio, chlorinated hydrocarbons are fairly easy to identify in the chromatograms of air pollutant mixtures by mass

chromatography of prominent chlorine containing fragments of the specific compounds.

The normal mass chromatogram is reconstructed by obtaining the ion current for a given ion from each mass scan stored in the computer memory over the entire GC-MS analysis. In a typical 3-second scan over a mass range of 1-300 amu the ion current measurement time for a given ion is only about 0.01 s. However, if the MS is tuned to this particular ion m/e value without scanning, the desired ion is detected continuously through the GC-MS analysis. By this technique, called selective ion monitoring (SIM), it is possible to obtain a 10 to 100-fold increase in sensitivity (98). Currently available GC/MS/computer systems can monitor several ions simultaneously in this way. It should be noted, however, that information from compounds not responding to this ion is lost. This essentially eliminates the use of this technique in analyses where only one sample is available.

# 11.6 SAMPLING AND ANALYSIS OF CHLORINATED HYDROCARBONS AS WATER POLLUTANTS

### 11.6.1 INTRODUCTION

Organic compounds can enter natural waters from a wide variety of sources. Surface waters may be contaminated by organic chemicals discharged in the waste effluents from various industries, run-off waters and natural degradation products.

Chlorinated hydrocarbons are present from industrial waste effluents and from the chlorination process used to disinfect both industrial and domestic sewage plant effluents, and also to disinfect raw intake waters used as sources of drinking water.

Methods of sampling water for chlorinated hydrocarbons have included solvent extraction (99), activated carbon adsorption followed by solvent extraction (100), head-space analysis (101) and inert gas stripping (102, 103).

Methods of analysis include gas chromatography (100-103), UV absorption (99), laser Raman spectroscopy (104, 105), and GC/MS/computer.

## 11.6.2 SAMPLING TECHNIQUES

The earliest sampling technique used for organic water pollutants was carbon adsorption. This method involves passing large volumes of water through a carbon column, drying the carbon, and then extracting it with selected organic solvents, usually chloroform and ethanol. However, this method gives poor recovery for volatile chlorinated hydrocarbons, and changes in flow rate through the cartridge produce changes in the

amounts of organic absorbed (106).

Liquid-liquid extraction methods using low or high boiling organic solvents followed by GC analysis have been described (107, 108). These methods have provided erratic or low extraction efficiencies for volatile compounds. In addition, large solvent responses and solvent impurities can cause serious chromatographic interferences.

Head space analysis techniques (100) have been employed for a number of years. With this method the sample is sealed in a partially filled container. Each volatile organic compound establishes an equilibrium between the gaseous and aqueous phase. At low concentrations, the ratio of concentrations between the gaseous and liquid phases is a constant (partition coefficient) and is unique for each compound. By analysing the gaseous phase and applying the appropriate partition coefficient the concentration can be calculated for each organic originally present in the aqueous phase.

A modification of this technique is inert gas stripping. An inert gas is sparged through the sample and the volatile organics are quantitatively transferred to the gaseous phase. These organics can then be trapped by adsorption and thermally desorbed to a GC for analysis. In this manner an analysis performed on the gas phase would have a direct relationship to the aqueous phase concentration.

Grob (109) developed a closed loop sparging system, which involved passing the purged head space gas through a micro-carbon filter and back through a 5 litre sample. Concentration factors of up to  $10^6$  were obtained for compounds up to  $\mathrm{C}_{24}$ . Bellar (102) used a 5 ml sample and the gas sparging technique to trap organics in drinking water on Tenax GC, and subsequently analysed the organics by thermal desorption into a

GC. A modification of this technique using a 1 ft. long Dexsil 300 and Tenax GC trap was used by Duholke and Meresz (110) to analyse organic compounds in St. Clair river water.

Sievers and co-workers (111, 112), in an ongoing research program to characterize the organic compounds present in domestic waste waters before and after treatment by chlorination and ozonization, routinely use gas sparging with nitrogen of volatile organics in a 0.5-1.5 l sample of water onto 60/80 mesh Tenax GC. The compounds are subsequently thermally desorbed into a GC and analysed by capillary GC/MS/Computer.

Although most efforts have been directed towards the inert gas stripping technique, considerable effort has been expended to develop new methods for directly adsorbing the organics from water. Burnham and co-workers have used Amberlite XAD resins for this purpose (113, 114). These researchers and Glaze (115) have made extensive use of Amberlite XAD-2 resin for the analysis of organic compounds in drinking water.

### 11.6.3 ANALYSIS TECHNIQUES

#### 11.6.3.1 DIRECT ANALYSIS TECHNIQUES

A number of researchers have reported success in direct analysis of polluted water. The use of laser Raman spectroscopy for detection and identification or organic compounds in water has been described (104, 105). This technique was investigated because of its advantages of unnecessary sample preparation and system portability. Application of this technique is, however, limited because of its low sensitivity and single component detection.

### 11.6.3.2 GAS CHROMATOGRAPHIC ANALYSIS

Direct aqueous injection of samples into the GC have been reported (110, 116, 117). Although these methods are generally useful for analysis of industrial effluents, the sensitivity is fairly low (around 1000 ng/l).

Until fairly recently, the analysis of concentrated samples by GC has been confined to the use of conventional packed columns. The use of GC-MS-computer techniques is necessary for analysis of complex mixtures containing chlorinated hydrocarbons. Such analyses have been reported by several investigators (102, 108-112).

Sievers and co-workers (111, 112, 118, 119) use glass capillary columns and Aue packings (92-95, 119, 120) to routinely analyse volatile organics in domestic wastewaters. Excellent separations are achieved, and mass spectra free of peak overlap and extraneous peaks from column bleed are obtained by the computer enhancement method devised by Biller and Biemann (98). Quantitative data are lost by this method (111), but good mass spectra for qualitative identification and analysis are obtained.

Jones et al (121) have reported a comprehensive analysis scheme for organic materials in process streams. The techniques utilized are liquid chromatography for class separation, followed by detailed analysis by HRMS, IR spectrophotometry, nuclear magnetic resonance (NMR) spectroscopy, high pressure liquid chromatography, and GC/MS. Such a unified approach to the analysis of polluted waters is necessary to obtain all possible data on the compounds present, including chlorinated hydrocarbons. However,

a considerable investment of expertise and instrumentation is required, which restricts the use of this approach to a few specialized laboratories.

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12 <u>ENVIRONMENTAL</u> <u>PERSISTENCE</u> <u>AND</u> <u>FATE</u>

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## 12.1 SUMMARY

The environmental fate of any substance depends on the medium in which it accumulates, and on the relative efficiencies of the various degradation pathways possible. For most of the compounds considered here the main degradation pathway is probably atmospheric photooxidation.

Studies have shown that, where these compounds are emitted in aqueous discharges, the half lives for evaporation are short. The actual half life depends, among other considerations, on the degree of turbulence in the aqueous phase. In any case, it does not exceed about seven hours.

There does not generally appear to be any significant accumulation of these compounds in sediments. Biological degradation of chlorinated compounds can take place, but this is a very slow process and does not compete with evaporation. Also, with the possible exception of chloroprene, hydrolysis and oxidation reactions do not take place at significant rates in the aqueous phase.

Atmospheric degradation can take place via photooxidation in the well known photochemical smogs. However, details of reaction mechanisms and products are not well understood. Photochemical smogs form when hydrocarbons and nitrogen oxides are mixed in ambient air and subjected to sunlight.

Intensive studies of these reactions have been carried out by a large number of research groups for several years, both in laboratory simulations, and in the ambient atmosphere. The chemistry alone is complex and requires consideration of hundreds of reactions, but in order to develop

a reliable predictive model, meteorological parameters must also be taken into account. Numerous mathematical models have been developed to relate pollutant emissions to ambient air quality through theoretical treatments of the chemical and physical processes taking place.

The chlorinated olefins of interest here are sufficiently reactive in the atmosphere that they can take part in photochemical reactions on a local scale. The other compounds, however, are much less reactive and are not expected to take part in photochemical smog formation on a local scale. Degradation of these less reactive chlorinated hydrocarbons takes place on a regional or global scale. The relative reactivities of various chlorinated hydrocarbons in the atmosphere have been studied by a number of workers. The compounds of interest here are listed below in order of decreasing reactivity. This ordering may vary somewhat from study to study depending on conditions used, etc. However, the general trends are as listed.

$$\begin{array}{l} {\rm CH_2} = {\rm CC1-CH} = {\rm CH_2} \ > \ {\rm CHC1} = {\rm CC1_2} \ > \ {\rm CHC1} = {\rm CHC1} \\ > \ {\rm CH_2} = {\rm CC1_2} \ > \ \emptyset - {\rm C1} \ > \ \emptyset - {\rm C1_2} \ > \ {\rm CC1_2} = {\rm CC1_2} \\ > \ {\rm CHC1_2-CHC1_2} \ > \ {\rm CH_2C1-CC1_3} \\ > \ {\rm CHC1_2-CH_2C1} \ > \ {\rm CHC1_3} \ > \ {\rm CH_2C1_2} \ > \ {\rm CH_2C1-CH_2C1} \\ > \ {\rm CH_3C1} \ > \ {\rm CH_3-CC1_3} \ > \ {\rm CC1_4} \\ \end{array}$$

In addition to industrial sources of chlorinated hydrocarbons through discharges, it has been demonstrated that organohalides can be formed during water treatment by chlorination. It appears that fulvic and humic acids may act as precursors. The yield of organohalides is reduced

at lower pH levels but also increases with time along the distribution system for potable water. In a number of US studies, it is reported that (in contrast to findings for raw water) the finished or treated water at all locations investigated contained chloroform in concentrations ranging from less than 0.1 to 311 ppb. In Ontario, studies have shown that, in potable water, chloroform was often the predominant organohalide and ranged from 1 ppb or less up to 159 ppb. Generally chloroform levels varied with different raw water sources. Ground-water generated the lowest concentrations of chloroform in finished water. The Great Lakes, which serve about 65 % of Ontario's population with drinking water, generated a relatively low level of chloroform while rivers and lakes had the highest.

The reported concentrations of organohalides in water courses are highly variable, however, elevated levels are usually associated with local industrial activity.

Numerous studies of ambient air concentrations of chlorinated hydrocarbons have been reported over the last few years. Much of this work has focused on the effect of chlorinated compounds on stratospheric chemistry. Global background concentrations as well as urban concentrations in heavily industrialized areas have been studied.

In the U.S., studies in a number of areas of high concentration of chemical and industrial activity report ambient concentrations of almost all of the compounds of interest here at levels ranging from ppt to ppb. Most compounds could be identified with a particular industrial activity near the sampling site. Similar results have been reported from studies in other countries.



Hemispheric background concentrations have been estimated for a number of chlorinated hydrocarbons. Significant concentrations for methyl chloride, methylene chloride, chloroform, carbon tetrachloride, methyl chloroform, trichloroethylene, and perchloroethylene are reported. Concentrations (in the northern hemisphere) range from 15 ppt for trichloroethylene to about 700 ppt for methyl chloride. It is of interest to note that methyl chloride is the largest carrier of chlorine in the atmosphere followed by carbon tetrachloride. Also, despite the relatively high atmospheric reactivity of tri- and perchloroethylene, they are still present in background air at concentrations of around 15-20 ppt due to their high volume usage.

With the exception of carbon tetrachloride, the other chlorinated hydrocarbons present in background air show strong inter-hemispheric gradients indicating significant anthropogenic sources. A large natural marine source of methyl chloride has been suggested. It is not clear whether or not carbon tetrachloride has a significant natural source. It has been speculated that chloroform, carbon tetrachloride and perhaps other chlorinated hydrocarbons may be formed through atmospheric reactions. There is no direct evidence to indicate that this does occur in the atmosphere.

## 12.2 INTRODUCTION

This chapter deals with, and evaluates, the various degradation pathways for the compounds of interest:

methyl chloride

dichloroethylene

methylene chloride

trichloroethylene

chloroform

tetrachloroethylene

carbon tetrachloride

chloroprene

dichloroethane

chlorobenzene

trichloroethane

dichlorobenzene

tetrachloroethane

In evaluating the environmental persistence and fate of a compound, it is necessary to determine the possible chemical and physical transformations which can occur, and to identify the relative importance of these transformations for each media within which the compound of interest may be found (eg air, water, soil, etc.). This data must then be combined with information on how readily the compounds are transferred from one medium to another in the environment, and where they are most likely to accumulate. Often, there are insufficient data from which all required parameters may be determined. Therefore, estimates and comparisons with similar compounds are frequently required. Environmental monitoring is essential to verify models, and provide information from which transport and transformation data may be derived.

In this chapter, the chlorinated hydrocarbons listed above are considered together, since they behave in a similar manner in the environment. Transport, transformations and measured ambient concentrations are considered both for air and water.

# 12.3 CHLORINATED HYDROCARBONS IN AIR

# 12.3.1 ATMOSPHERIC TRANSPORT AND TRANSFORMATION

Once emitted to the atmosphere chlorinated hydrocarbons are subject to transport, dispersion, transformation, and deposition via complex physical and chemical processes. Governing factors include meteorological conditions such as wind speed, mixing height, temperature, relative humidity, turbulence intensity, atmospheric stability and solar intensity. Ground surface characteristics in conjunction with meteorological conditions affect the deposition rate to the earth for various pollutants. Chemical and physical transformations are also affected by the presence of other atmospheric pollutants.

Apart from concerns over possible direct toxic effects of chlorinated hydrocarbons, which for most of these compounds, would only be important in areas near major sources, research efforts have been directed towards an understanding of the role these compounds play in the formation of photochemical smogs and in the global balance of chlorinated compounds.

Chlorinated ethylenes, chloroprene, chlorobenzene and possibly dichlorobenzene are all sufficiently reactive in the atmosphere that they may be important in the formation of photochemical smogs in urban and nearby rural areas. Chlorinated methanes, and ethanes, however, are much less reactive and therefore would be widely dispersed in the atmosphere before chemical reactions take place.

For these very stable compounds the concern is that, once released to the lower atmosphere (troposphere), their lifetime is long enough that

they will eventually be transported to the stratosphere where, due to the larger ultra-violet radiation flux at that height, they can be photolytically decomposed releasing chlorine atoms. These released C1 atoms can then take part in a series of chain reactions involving ozone and other chemical species. The net result could be a reduction in the steady state concentration of  $0_3$  in the stratosphere and this would lead to an increase in the flux of ultra-violet radiation to the surface of the earth, which would normally be filtered out by  $0_3$ .

The actual effects of the release of these stable chlorinated hydrocarbons to the troposphere are difficult to calculate and require the use of complex chemical, physical, and meteorological mathematical models. The possible consequences of increased ultra-violet radiation to the earth's surface on weather, human health, animals, and vegetation, etc. are difficult to predict with any degree of certainty.

Since Rowland et al, 1975 (1) published their theory indicating the possibility that some very persistent chlorinated hydrocarbons could effect the dynamically balanced levels of  $0_3$  in the stratosphere, a large number of experimental and theoretical studies have been carried out to test their hypothesis. While it now appears that some of these persistent compounds are in fact reaching the stratosphere, the resulting effect on  $0_3$  levels in the stratosphere and the possible secondary effects are still the subject of much study and debate.

Despite this the governments of Canada and U.S.A. have both moved to restrict the "non-essential" use of the compounds  $CF_2Cl_2$  and  $CFCl_3$ .

The more reactive chlorinated ethylenes are likely to contribute, along with other hydrocarbons, to the formation of photochemical smog. There are few reported studies of the photochemistry of chlorinated ethylenes and their participation in the formation of photochemical smogs. However, a great deal of work has been carried out using a variety of other hydrocarbons thought to be important in smog formation. A general review of some of this work is outlined below.

It is an interesting paradox that, starting with contaminants in the atmosphere such as NO, SO<sub>2</sub> and hydrocarbons which have no oxidizing power, the end result of sunlight is the production of a powerful oxidant smog with oxidizing agents such as peroxyacyl nitrates and ozone, etc. Air Quality Simulation

Numerous mathematical models have been developed to relate pollutant emissions to ambient air quality through theoretical treatments of the chemical and physical processes taking place in the polluted atmosphere: Eschenroeder et al, 1972 (2), Demerjian et al, 1974, 1976, 1977 (3, 4, 5), Reynolds et al, 1974 (6), Niki et al, 1972 (7), Hecht et al, 1972 (8), and others.

Such air quality simulation models find application in:

- indicating areas where further research is needed
- development of environmental legislation
- development of implementation planning
- impact assessment
- source identification



- monitor siting
- transportation and land use planning
- episode control systems

The models vary in their complexity from relatively simple ones, in which only a limited number of chemical reactions are considered in static systems, or where only first order chemical processes are considered along with simple diffusion models, to the complex models involving dynamic systems incorporating time dependent emissions and solar radiation flux, hundreds of chemical reactions and detailed dispersion calculations. The complex models require large computers to handle required calculations.

Most of the information available today, related to the chemistry of the polluted atmosphere, is derived from laboratory experiments and smog chamber studies using rather simple analogues to the complex atmospheric mixtures. At the present time, our understanding of the reaction mechanisms in rather simple static systems (eg C<sub>2</sub>H<sub>6</sub>, and NO in air irradiated in a smog chamber over 6 to 8 hours) is quite good. Experimental data and computer generated concentration profiles are in good agreement (Figure 12-1).

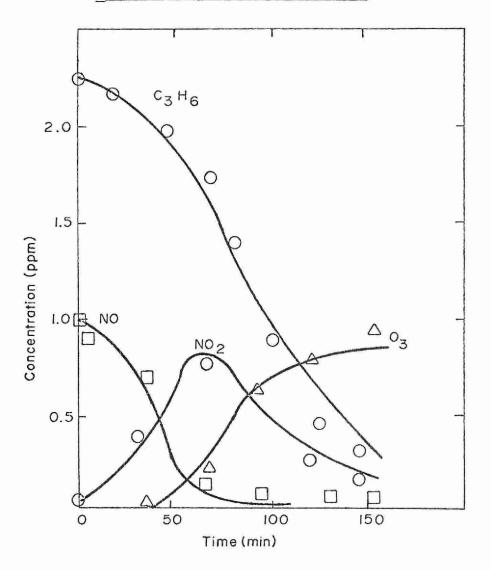
Even with a "simple" system such as propylene photooxidation, a large number of reactions must be considered. Hecht et al, 1972 (8) have had success describing this system using a mechanism comprised of 81 reactions:

- a) 19 reactions on the  $NO-NO_2-O_2-CO-H_2O$  system
- b) 19 reactions for the oxidation of propylene by 0 and 0 $_3$
- c) 16 reactions for attack on propylene by OH

# FIGURE 12-1

# CONCENTRATION CHANGES ON IRRADIATION OF A

MIXTURE OF  $(NO + NO_2 + C_3H_6)$ 



Solid line - calculated Points - experimental data (Niki et al, 1972 (7)) 1

- d) 13 reactions for formation and destruction of peroxynitrates
- e) 8 reactions for decomposition of aldehydes
- f) 6 additional reactions involving free radicals

In a very detailed review, Demerjian et al, 1974 (3) list over 450 reactions and rate constants thought to be important in atmospheric chemistry. No aromatic compounds were considered. The complexity of atmospheric photochemical reaction systems stems partly from the multiplicity of organic pollutant species, partly from the large numbers of possible elementary reactions, and partly from the difficulties of observation and analysis of components, products, and intermediate compounds at the very low concentrations encountered.

Despite these difficulties, there is a reasonable degree of qualitative agreement between air quality simulations and observed diurnal variations of the major components of photochemical smog. Studies following reactions in well defined air parcels have been reported by Calvert, 1976 (9), Westberg et al, 1974 (10) and Polgar et al, 1976 (11). Generally, good qualitative agreement with simulations is confirmed although further work is needed for hydrocarbons of low reactivity. These include many of the chlorinated hydrocarbons, light paraffins and aromatics.

A considerable amount of effort has been devoted to studies of highly reactive hydrocarbons such as internally double bonded olefins, but very little to the less reactive compounds. However, consideration of less reactive compounds is now thought to be important because:

- long-range transport of  $0_3$  and its percursors may be

responsible for elevated rural concentrations of  $0_3$ 

- serious pollution episodes have resulted from the occurrence of meteorological conditions which lead to multi-day stagnant air conditions (and persistent high 0<sub>3</sub> levels) in which ambient air contains not only each day's fresh pollutant burden but also "aged smog" carryover from the previous days

Under these conditions a number of compounds previously cited as nonreactive such as benzene, propane, n-butane, etc. can react to produce substantial amounts of  $0_3$ .

# General Chemistry of Hydrocarbon/NO<sub>X</sub> Systems

In mixtures of hydrocarbons, NO and clean air,  $NO_2$ , will slowly form by:

$$2NO + O_2 \rightarrow 2NO_2$$
 (1)

Once a small amount of  $NO_2$  is present it can absorb light and dissociate:

$$NO_2 + hv \rightarrow NO + O$$
 (2)

Since  $0_2$  is present in relatively large concentrations in air,  $0_3$  formation is the predominant reaction of 0 atoms formed in (2):

$$0 + 0_2 + M \rightarrow 0_3 + M \tag{3}$$

(M refers to any deactivating third body)

Ozone will rapidly react with NO to form  $NO_2$  again:

$$NO + O_3 \qquad \rightarrow \qquad NO_2 + O_2 \tag{4}$$

Reactions (2)-(4) produce no net change. However, as long as the irradiation is maintained the system must contain a small steady state concentration of  $0_3$  and 0 atoms.

Occasionally 0<sub>3</sub> and 0 atoms will react with hydrocarbons present to form organic free radicals. These free radicals rapidly combine with 0<sub>2</sub> forming peroxyhydrocarbons which can react with other hydrocarbons or NO. The result of these secondary free radical reactions is the formation of compounds such as aldehydes; ketones; alkyl, acyl and peroxyacyl nitrates; hydrogen peroxide; organic peroxides; nitrous, and nitric acids. These secondary compounds can absorb light and dissociate forming more free radicals which then react further.

The net result is the generation of a large number of secondary products and radicals from chain reactions involving free radical mechanisms. Some of these secondary products may have significant inhalation toxicities to man. Other effects such as visibility reduction, materials damage, etc. may also be important.

The identity of the intermediate species which propagate the chains is a subject of much interest as well as theoretical importance. These intermediates may be viewed as providing the "driving force" for the photo-oxidation of hydrocarbons and thus for the development of photochemical smog. At present the OH radical is believed to be the most important intermediate assigned this role during at least the early stages of photochemical smog formation (3, 12, 13, 14).

In urban areas where photochemical smogs are prevalent, the following sequence of events, on a diurnal cycle, is commonly observed.

#### Predawn Hours

urban activity and emissions at a minimum, primary air
 contaminants are carbon monoxide, nitric oxide and hydrocarbons

- secondary contaminants such as  $0_3$ ,  $N0_2$ , etc. remain at low levels in the absence of photochemical reactions

## Sunrise

- increasing activity increases the accumulation of primary air contaminants
- not much photochemical activity until the sun is fairly high  $\hbox{Two Hours After Sunrise}$ 
  - daily injection of NO and hydrocarbons is well under way
  - $NO_2$  and some secondary products such as aldehydes and ketones start to appear

## Four Hours After Sunrise

- NO has been reduced to a low level as it has been converted to  $\mathrm{NO}_2$
- $\mathrm{NO}_2$  has reached a peak value
- other secondary products such as aldehydes and ketones, etc.
   continue to increase
- hydrocarbons have peaked and are starting to decrease
- ozone has just begun to appear
- the appearance of  $^{0}_{3}$  coincides with the disappearance of NO

# Early Afternoon Hours

- $0_3$  reaches a maximum and begins to slowly decline
- as  $0_3$  builds to its peak,  $N0_2$  decreases to a low level
- some of the earlier formed secondary products begin to decline
   (eg aldehydes)



- hydrocarbons continue to decline

# Late Afternoon Hours

- afternoon injection of NO from traffic scavenges the remaining traces of  $\mathbf{0}_3$
- hydrocarbons continue to decline to low levels
- NO and NO  $_{2}$  are both present at fairly low levels

As already mentioned above, chlorinated ethylenes are sufficiently reactive to be important in the generation of photochemical smog. Chlorinated methanes and chlorinated ethanes are too stable to be of consequence in photochemical smog generation, although, from a global standpoint, their presence may be significant to the extent that stratospheric chemistry and  $0_3$  concentrations may be effected. Measured concentrations of these compounds are presented in the following Section 12.3.2.

The most important tropospheric sink for the chlorinated hydrocarbons considered here is probably attack by OH radicals. Cox et al, 1976 (15) report a technique for the determination of relative rates of attack by OH on hydrocarbons, using the photolysis of nitrous acid in air as a source of OH as in reaction (5):

$$HONO + hv \rightarrow NO + OH$$
 (5)

In the presence of hydrocarbons reactions (6)-(8) may take place:

$$OH + RH \qquad \rightarrow \qquad H_2O + R \cdot \tag{6}$$

$$R^{\bullet} + O_{2} \rightarrow RO_{2}^{\bullet}$$
 (7)

$$RO_2 \cdot + NO \rightarrow NO_2 + RO \cdot$$
 (8)

An alternative decay path for OH is:

$$0H + HONO \rightarrow H_2O + NO_2$$
 (9)

The extent of  $NO_2$  formation with and without hydrocarbons present can be related to the relative reactivity of OH towards RH and HONO. Reactivities were found to decrease in the order:

$$CHC1_3 > CH_2C1_2 > CH_3C1 > CH_3-CC1_3 > CH_4 >> CC1_4$$

By estimating an atmospheric half life for  $\mathrm{CH}_4$  of 4.5 years the half lives for the other compounds can be estimated (Table 12-1).

From these data Cox et al, 1976 (15) conclude that CCl<sub>4</sub> is essentially inert towards OH attack and it's major sink is photolysis in the stratosphere. The other chlorinated hydrocarbons in Table 12-1 would be expected to react with OH in the troposphere as a major sink.

Chlorinated methanes are apparently more reactive than chlorinated ethanes. Furthermore, in view of the reactivities and observed ambient background concentrations of methylene chloride, methyl chloride and methyl chloroform it is concluded that there must be significant natural sources of these compounds in addition to anthropogenic sources.

In an earlier study Lillian et al, 1975 (16) report photochemical experiments in simulated atmospheres with a number of chlorinated hydrocarbons. They found that there was essentially no loss in concentration of carbon tetrachloride or methyl chloroform over irradiation periods of up to 200 hours. Under similar conditions the half life for perchloroethylene was about seven hours. It is interesting to note here that phosgene was a major product.

TABLE 12-1

# HALOCARBON REACTIVITIES WITH OH

HALOCARBON	$\frac{K_{OH}}{(cm^2 s^{-1} \times 10^{14})}$	LIFETIME (years)
снс 1 3	16.8	0.19
CH <sub>2</sub> C1 <sub>2</sub>	10.4	0.30
сн <sub>3</sub> с1	8.5	0.37
CH3-CC13	2.8	1.1
СН4 .	0.7	4.5
cc1 <sub>4</sub>	<10 <sup>-2</sup>	>330

Assumes  $[OH] = 10^{-6}$  molecules cm<sup>-3</sup>.

Dilling et al, 1976 (17) report decomposition rates of a number of chlorinated and other hydrocarbons in simulated atmospheres in the presence of NO and bright sunlight. Some of the half lives determined are summarized in Table 12-2. They also found that the presence of other hydrocarbons reduced the decomposition rate of several chloroethylenes. The half life of 1,1,2-trichloroethane of only about 16 hours is rather short and faster than expected based on studies of OH attack rates.

Several studies have recently been reported which measure directly the rate constants of OH reactions with a number of hydrocarbons and chlorinated hydrocarbons (18-22).

These studies and other work have been reviewed by Pitts et al, 1977 (22) and presented in the form of a five class reactivity scale based on the rate constant of OH attack on the hydrocarbon. The value of this approach is based on the assumption that the first step in atmospheric degradation for most organic compounds is attack by OH.

Thus, the lifetime of the compound of interest, before chemical transformation, is related to the rate at which it reacts with OH, and only those chemicals which undergo such reactions at a significant rate are of consequence with respect to secondary effects.

Thus such a scale can indicate the <u>potential</u> that various compounds have for the formation of photochemical smog. If, however, the criteria being considered is the <u>degree</u> to which secondary effects are manifested, then this reactivity scale is inadequate since a consideration of reaction mechanisms and products beyond the primary step is needed.

# TABLE 12-2

# PHOTODECOMPOSITION RATES OF CHLORINATED AND OTHER HYDROCARBONS UNDER SIMULATED ATMOSPHERIC CONDITIONS

COMPOUND	HALF LIFE (hours)
Methyl chloroform	>>1700
Methylene chloride	>250
1,1,2-trichloroethane	15.9
Perchloroethylene	14.2
Chlorobenzene	8.7
Toluene	6.8
Ethylbenzene	5.0
Trichlorobenzene	3.5
p-Xylene	3.1
m-Xylene	2.9
1,2-dichloroethylene	2.9
Vinylidene chloride	2.1

Table 12-3 lists the classification of a large number of organic compounds including the chlorinated hydrocarbons of interest here. Each class is based on an order of magnitude difference in reactivity of the compound towards OH. Class I is the least reactive and contains methane, chloromethane, carbon tetrachloride and methyl chloroform. Class II contains dichloromethane, trichloromethane, and 1,2- and 1,1-dichloroethane. Although chlorinated ethylenes are listed, they would be expected to fall within the more reactive classes IV or V.

Global budgets for compounds of low reactivity are useful in evaluating probable sources and sinks. The inventories of sources and sinks for a given compound should be in balance with measured atmospheric burdens. Singh et al, 1977 (23) point out that the background concentration of methyl chloride of about 700 ppt is significantly higher than other halocarbons. For an estimated atmospheric lifetime of less than one year and current estimates of anthropogenic emissions, large natural sources are indicated. Zafiriou, 1975 (24) has suggested that the reaction of methyl iodide and chloride ions in seawater would provide a sizable natural source of methyl chloride. The observed concentrations of methyl iodide by Lovelock et al, 1973 (25) in the sea are consistent with a large marine source of methyl chloride. Other sources such as microbial fermentation, and combustion of vegetation have also been suggested, Palmer, 1976 (26). It is also possible that secondary formation of methyl chloride may take place in the atmosphere. Decomposition of ethylene chloride or vinyl chloride could yield some methyl chloride (27).



## TABLE 12-3

# REACTIVITY CLASSIFICATION BASED ON REACTION

# WITH THE HYDROXYL RADICAL

#### CLASS 1 (<4.8×107) 0

Trifluorquethane 1,1,2-Tricaloro-1,2,2-trifluoroethane Tetraf luore sethane 1,2-Dichlero-1,1,2,2-tetrafluoroethane Chlorotrif !uoremethane Dichlorod ( lucromethane Fluorottich!eromethane 1-Chloro-1, r-difluoroethane Tetrachioromethane Difluoromethane Methane 2-Chloro-1,1,1-trifluoroethane 2-Chloro-1,1,1,2-tetrafluoroethane 1,1,1-Trich!oroethane Fluoromethane Dicalordi Loromethane 2,2-Dichtyen-1,1,1-trifluoroethane 1.1-Diffuoroethane Chlorofluoromethane Btomomethicse Chloromethane Chlorodificoromethane

#### CLASS 11 (4.8×107-4.8×108) a

Trichloromethane
Dichloromethane
Carbon monoxide
Anmonia
Accetylene
1,2-Dichloroethane
Ethane
1,1-Dichloroethane
Chloroethane

#### CLASS 111 (4.8×108-4.8×109) 3

Neopentane Methanol Methylacetylene 2,2,3,3-Tetramethylbutane Cyclobutane Benzene Isobutane Propane n-Sutane Ethanol Methyl ethyl ketone Isopentane 1-Propanol 2,2,4-Trimethylpentane 2,2,3-Trimethylbutane n-Propyl acetate Allene 2,3-Dimethylbutane Hydrogen Sulfide 2-Methy Ipentane sec-Butyl acetate Toluene Cyclopentane n-Propy Ibenzene Isopropylbenzene n-Hexane n-Pentane p-Monthane 1-Butanol Cyclohexane 2-Propanol 4-Methyl-2-pentanol 3-Nothy Ipentane Ethene

## CLASS IV (4.8×10<sup>9</sup>-4.8×10<sup>10</sup>)a

Ethylbenzene n-Oxtane Diethyl ether p-Xylene p-Ethylloluene o-Ethyltoluene o-Xylene Tetrahydrofuran Methyl isobutyl ketone p-Cymene di-n-propyl ether m-Ethyltoluene Methoxybenzene Methylamine m-Xylene 1,2,3-Trimethylbenzene Dilsobutyl ketone Propene 3,3-Dimethy1-1-butene 1-Pentene 1-Hexene 1,2,4-Trimethylbenzene Methyl mercaptan o-Cresol 1-Butene 1-Heptene 1.3.5-Trimethylbenzene Isobutene cls-2-Butene 2-Methy I-1-butene a-Pinene cis-2-Pentene B-Pinene trans-2-Eutene Cyclohexene 1,3-Butadiene Isoprene

## CLASS V (24.8×1010) a

2-Methyl-2-butene
3-Carene
1-Methylcyclohexene
8-Phellandrene
Carvomenthene
d-Limonene
2,3-Dimethyl-2-butene
Dihydromyrcene
Myrcene
cis-Ocimene

Range of values (in liter mole | sec |) for the rate constant for reaction of the OH radical with the listed compounds.

Anthropogenic emissions of methylene chloride are the largest of all chlorinated methanes (27). However, there are very few reported measurements of background concentrations and therefore it is difficult to judge whether or not natural sources are important. Cox et al, 1976 (15) conclude that industrial output of methylene chloride is probably insufficient to balance a sink due to 0H attack. However, they note that observed hemispheric concentration differences are consistent with an anthropogenic source.

The relative contribution of natural and anthropogenic sources to the atmospheric burden of chloroform has not yet been resolved. Historical emission inventories for chloroform are not available. Measured concentrations near oceans and in sea water indicate a marine source. Whether this is due to natural production or production by marine organisms or simply to the degradation of anthropogenic precursors, such as carbon tetrachloride, trichloroethylene, perchloroethylene or methyl chloroform, is uncertain (27). Graedel et al, 1976 (28) have concluded that atmospheric formation of chloroform and other chlorinated hydrocarbons is negligible.

Information on carbon tetrachloride is more complete than for any other chlorinated hydrocarbon. Recent publications dealing with global balances for carbon tetrachloride have concluded that most of the observed carbon tetrachloride in the atmosphere can be accounted for from anthropogenic sources; Altshuller, 1976 (29), Singh et al, 1976 (30), Galbally, 1976 (31), National Research Council (U.S.), 1976 (32). The agreement over the sources of carbon tetrachloride in the atmosphere appears to be fortuitous, however, since quite different data sets were used. Estimated background concentrations used varied from 60 to 160 ppt,



average atmospheric lifetimes from 18 to 100 years, and anthropogenic source strengths varied by over a factor of two.

Of the chlorinated ethanes, methyl chloroform is by far the most stable and has received most of the attention in the literature. In a study of methyl chloroform reaction rate with OH, Cox et al, 1976 (15) conclude that industrial output is probably insufficient to balance the sink due to OH attack. Other authors, however, conclude or assume that the only source of methyl chloroform in the atmosphere is anthropogenic; Lillian et al, 1975 (16), Singh et al, 1977 (23), McConnell et al, 1978 (33). The half life in the atmosphere is estimated to be between one and eight years. McConnell et al, 1978 (33) estimate that up to 15% of emitted methyl chloroform may reach the stratosphere.

Chlorinated ethylenes are likely to have a minimal stratospheric impact due to their high reactivity. It is estimated that only about 2.4 % of perchloroethylene and 0.4 % of trichloroethylene emitted reach the stratosphere, Singh et al, 1977 (23).

## 12.3.2 MEASURED AMBIENT AIR CONCENTRATIONS

Reports in the literature of measurements of chlorinated hydrocarbons in ambient air have only appeared over the last seven years, in parallel with the development of sampling and analytical techniques having the required sensitivity and selectivity.

Most of this work has focused on the contamination of the atmosphere with chlorinated hydrocarbons on a global scale and has dealt with compounds of high stability in the lower atmosphere (troposphere). The concern is that these highly stable compounds, once released to the

troposphere, eventually are transported to the stratosphere where, due to the increased ultra-violet radiation, they are photolytically decomposed. The compounds under consideration here, which could be important in stratospheric chemistry, are carbon tetrachloride and perhaps methyl chloroform.

Studies have also been reported by a number of workers dealing with the distribution of several chlorinated hydrocarbons on a regional scale in rural, urban, and heavily industrialized areas. The compounds most often reported include carbon tetrachloride, trichloroethylene, perchloroethylene, and methyl chloroform.

Pellizzari, 1978 (34) has recently reported the results of a comprehensive broad spectrum chemical survey of volatile organic vapors in ambient air from several geographical areas in the continental U.S.A. The areas selected for study include Houston, TX, Baton Rouge, LA, and a site in New Jersey. These areas were chosen because of their high concentration of chemical and industrial activity.

More than 100 compounds were identified including a wide range of chlorinated hydrocarbons, as would be expected, at the sites studied. The observed concentrations were highly variable depending on the prevailing meteorological conditions and the site chosen. The data are pooled and average results are presented in Table 12-4. The compounds are divided into three groups. The first group, which includes methylene chloride, chloroform, carbon tetrachloride and perchloroethylene, lists these compounds which were always found at all of the sites sampled. The second group includes compounds frequently found to be present at most sites and the third group includes those compounds which were infrequently



# TYPICAL CONCENTRATIONS OF CHLORINATED HYDROCARBONS IN AMBIENT AIR NEAR HIGHLY INDUSTRIALIZED

# AREAS OF THE U.S.A.

GROUP	COMPOUND	AVERAGE CONCENTRATION (ppb)
Α	Methylene chloride	11.0
А	Chloroform	1.8
Α	Carbon tetrachloride	0.5
Α	Perchloroethylene	0.4
В	1,2-dichloroethane	2.0
В	Methyl chloroform	1.0
В	Trichloroethylene	1.0
В	Chlorobenzene	0.1
В	Dichlorobenzene (ortho)	0.5
С	Methyl chloride	0.5
С	l,l-dichloroethane	2.4
С	1,1,2-trichloroethane	0.6
С	1,1,1,2-tetrachloroethane	0.003
С	1,1,2,2-tetrachloroethane	0.004
С	l,l-dichloroethylene	0.5
С	Chloroprene	0.6

found and only at some sites.

It can be seen from the raw data that a number of these compounds are clearly identified with the particular industrial activity near the sampling site. Chloroprene and chloro- and dichlorobenzene are good examples. However, no meteorological evaluation or source identification was attempted for the data.

Correia et al, 1977 (35) report the results of a study to determine the occurrence of methyl chloroform, and tri- and perchloroethylene in a number of western European countries. These compounds were found to be present at low levels at all of the sampling sites chosen. Climatic conditions such as wind speed and direction, precipitation, etc. were found to have a significant effect on observed concentrations as would be expected. Table 12-5 summarizes their results.

In a study of ambient air in Tokyo, Ohta et al, 1976 (36) report annual average concentrations of carbon tetrachloride, methyl chloroform and tri- and perchloroethylene. The observed concentrations of these compounds depended on meteorological conditions. The distribution of carbon tetrachloride, methyl chloroform, and trichloroethylene concentration peaks coincided with expected sources such as metal products plants and chemical industries. However, perchloroethylene was distributed rather evenly.

The ratio of the observed annual average concentration for each compound and its estimated annual emission was calculated. These were about the same for methyl chloroform, and tri- and perchloroethylene but the ratio for carbon tetrachloride was a factor of 1000 times higher



TABLE 12-5

# AMBIENT AIR CONCENTRATIONS OF CHLORINATED

#### HYDROCARBONS IN A NUMBER OF WESTERN

# EUROPEAN COUNTRIES

COUNTRY	METHYL CHLOROFORM	CONCENTRATION (ppb) TRICHLOROETHYLENE	PERCHLOROETHYLENE
United Kingdom	0.03 - 1.0	0.17 - 3.40	<0.01 - 1.35
Holland	<0.02 - 0.13	<0.02 - 0.17	0.01 - 0.13
Denmark	ND - 6.55	0.17 - 8.5	ND - 3.38
Belgium	ND - 0.39	0.17 - 1.36	0.14 - 1.22
France	<0.84 - 2.0	0.17 - 8.15	0.07 - 5.0
Italy			0.27 - 1.35

ND - Not Detected

(Table 12-6). It seems unlikely that this puzzling result could be due to global background levels of carbon tetrachloride since they are generally accepted to range from about 0.06 ppb up to 0.15 ppb. Further study is needed here.

Singh et al, 1977 (23) report urban and rural concentrations of a number of compounds including methyl chloride, chloroform, carbon tetrachloride, methyl chloroform, and tri- and perchloroethylene, as found at several coastal and inland sites in California.

They report "clean air" background concentrations found in desert sites or from the averages of the lower 50 % of measurements made at coastal sites. All of the compounds listed above were found to be present at every site studied. Results from the data of all sites are summarized in Table 12-7.

Carbon tetrachloride showed the least variation with the estimated background concentration of 115 ppt only about 10 % lower than the average of all sites sampled. The maximum concentration observed was only 290 ppt. No gradients between sites or seasonal variations were found. It was pointed out that a possible secondary source of carbon tetrachloride could be the heterogeneous decomposition of CCl<sub>3</sub>COCl which is a product of perchloroethylene photooxidation.

Both methyl chloride and chloroform showed significant concentration gradients between marine and continental air masses which was interpreted to indicate a marine source. In the case of chloroform this was attributed to coastal water contamination.



# ANNUAL AVERAGE CHLORINATED HYDROCARBON

# CONCENTRATIONS IN TOKYO

CHEMICAL	CONCENTRATION AVERAGE	CONCENTRATION AVERAGE ESTIMATED EMISSIONS (ppb/ton)
Carbon Tetrachloride	1.4	$23 \times 10^{-2}$
Methyl Chloroform	0.8	$1.6 \times 10^{-5}$
Trichloroethylene	1.2	1.1 × 10 <sup>-5</sup>
Perchloroethylene	1.2	$2.1 \times 10^{-5}$

TABLE 12-7

CHLORINATED HYDROCARBON CONCENTRATIONS

MEASURED IN CALIFORNIA (ppt)

COMPOUND	MAXIMUM	MINIMUM	AVERAGE	ESTIMATED BACKGROUND
Methyl chloride	2130	645	1060	710
Chloroform	880	10	50	17
Carbon tetrachloride	290	105	125	115
Trichloroethylene	5500	10	120	15
Perchloroethy lene	3700	15	300	30

Methyl chloroform and tri- and perchloroethylene are primarily of anthropogenic origin. Therefore it is not surprising that background concentrations are rather low in comparison to the range of observed concentrations at each site. The relatively high reactivity of tri- and perchloroethylene explains the low background concentrations observed for these compounds.

Pearson et al, 1975 (37) report the analysis of air samples from various locations in England which include a site near an organochlorine manufacturing plant in Runcorn, Cheshire. The compounds chloroform, carbon tetrachloride, trichloroethane, and tri- and perchloroethylene were found to be present at all of the sites where samples were taken. The observed concentration levels of carbon tetrachloride and chloroform were higher than expected for anthropogenic sources alone since estimated emissions for these compounds in industrial processes is small. The observations are summarized in Table 12-8. Lovelock et al, 1973 (38) have also reported that the observed concentrations of carbon tetrachloride over the Atlantic Ocean are in excess of that which could be expected to arise from purely anthropogenic sources. He suggests that a reaction between methane and chlorine in the troposphere could produce carbon tetrachloride. It is possible chloroform could also be formed in this way. There is no direct evidence at present to indicate that these reactions do take place in the atmosphere.

Lillian et al, 1975 (16) report concentrations of a number of chlorinated hydrocarbons at various geographical sites and under different

TABLE 12-8

CHLORINATED HYDROCARBONS IN AMBIENT

AIR IN ENGLAND (ppb)

LOCATION	PERCHLORO- ETHYLENE	TRICHLORO- ETHYLENE	TRICHLORO- ETHANE	CARBON TETRA- CHLORIDE	CHLOROFORM
Runcorn Works perimeter	15-40	40-64	∿16	10-70	10-40
Runcorn Heath	0.2-5	12-42	6.2-11	2.5-8	<0.1-3.6
Liverpool/Manchester suburban area	<0.1-10	1-20	<0.1-6	1-20	3-8
Moel Famau, Flintshire	<0.1-2.5	1-9	2-4	0.7-3	<0.1-0.4
Rannoch Moore, Argyllshire	0.3-1	2.5-8	1-1.5	4-5	0.1-0.5
Forest of Dean, Monmouthshiret	3	5	3.8	0.4	9

† Single sample

meteorological conditions in the U.S. Carbon tetrachloride and methyl chloroform were found to be present in all samples at all sites in sub-ppb concentrations. Tri- and perchloroethylene were found at least 50 % of the time at all sample sites and were generally present at concentrations in excess of 60 ppt. Chloroform was only found at those sites where a reasonable source could be invoked. Average concentrations reported for some of the sites are summarized in Table 12-9.

In a study directed to finding a suitable Los Angeles air mass label, Simmonds et al, 1974 (39) measured concentrations of chloroform, carbon tetrachloride, methyl chloroform, and tri- and perchloroethylene in air over the Los Angeles basin. Average concentrations were found to be 0-22 ppb for carbon tetrachloride, 0.37 ppb for methyl chloroform and 1.25 ppb for perchloroethylene. These compounds were found in all samples. Carbon tetrachloride show the least variation in concentration with more than 86 % of all measurements falling within the range 0.1 to 0.3 ppb. Chloroform and trichloroethylene were found infrequently and with a considerable variation in concentration. There was, generally, a decrease in concentrations for all compounds on moving from the in-land valleys to the coast.

Global background concentration measurements of a number of halogenated hydrocarbons have been reported by Cox et al, 1976 (15). Separate estimates are made for the Northern and Southern Hemispheres. Southern Hemispheric data are from a series of samples taken at Blouberg seashore near Cape Town, S. Africa, while Northern Hemispheric measurements were made at Adrigole, Ireland and at Bowerchalke, Wiltshire, U.K. (see Table 12-10).

AVERAGE CHLORINATED HYDROCARBON CONCENTRATIONS

AT SEVERAL EASTERN U.S.A. LOCATIONS (ppb)

LOCATION	CHLOROFORM	TRICHLORO- ETHYLENE	PERCHLORO- ETHYLENE	METHYL CHLOROFORM	CARBON TETRACHLORIDE
New York, N.Y. (urban)	<0.01	0.11	1.2	0.28	0.38
White Fall Mountain	ns <0.01	<0.02	0.09	0.083	0.24
Sandy Hook, N.J. (over ocean)	<0.01	0.18	0.73	0.18	0.28
Seagirt, N.J.	<0.01	<0.02	0.25	0.072	0.19
Wilmington, Delawa (above inversion)		<0.02	<0.02	0.025	0.10
Wilmington, Delawar (below inversion)		0.075	0.73	0.065	2.1

TABLE 12-10

# GLOBAL BACKGROUND CONCENTRATIONS OF CHLORINATED HYDROCARBONS (ppt)

COMPOUND	S. HEMISPHERE (1974)	N. HEMISPHERE (1974)
Methyl chloride		690 (390)
Methylene chloride		35(18.8)
Chloroform	<3	26.5(7.7)
Carbon tetrachloride	68.9(3.7)	110.9(10.7)
Methyl chloroform	24.4(2.8)	64.8(17.2)
Trichloroethylene	1.5(1.2)	15(12.1)
Perchloroethylene		27.6(9.3)

S.D. given in parenthesis

(--) indicates no measurement made

With the possible exception of carbon tetrachloride, there is a marked higher concentration for the compounds measured in the Northern Hemisphere over that in the Southern Hemisphere. It is of interest to note that methyl chloride is the largest carrier of chlorine atoms in the troposphere with carbon tetrachloride the next largest.

In a recent study reported by Sandalls et al, 1977 (40) ambient levels of carbon tetrachloride were measured by aircraft over the British Isles. The "clean air" background concentrations were reported as about 60 ppt. This concentration is similar to that reported by Lovelock et al, 1973 (38) over the Atlantic Ocean. However, Lovelock, 1974 (41) later reported average background levels of 137 ppt and Wilkniss et al, 1975 (42) reported concentrations of 258 ppt over the Arctic Ocean. Cox et al, 1976 (15) reported average background concentrations of 111 ppt over the ocean off the Irish coast. There does not appear to be any obvious reason for these variable results for background carbon tetrachloride concentrations.

#### 12.4 CHLORINATED HYDROCARBONS IN WATER

#### 12.4.1 CHLORINATED HYDROCARBONS FROM WATER CHLORINATION TREATMENT

Chlorine is widely used in the treatment of drinking waters, sewage effluents, industrial cooling waters and swimming pools, etc. The primary purpose of the treatment in all cases is the destruction of pathogenic bacteria and other micro-organisms and the control of color and taste. It has also been shown by Ingols et al, 1963 (43) that addition of chlorine to sewage effluent can reduce the BOD of the effluent in excess of the chemical oxidizing potential of the chlorine used.

Normally chlorine is added to the water to be treated either in its elemental form, Cl2, or as a hypochlorite salt. In solution an equilibrium is established via reactions (1) and (2) below.

$$C1_2 + 2H_20$$
  $\stackrel{?}{\leftarrow}$   $H0C1 + H_30^+ + C1^-$  (1)  
 $H0C1 + H_20$   $\stackrel{?}{\leftarrow}$   $H_30^+ + 0C1^-$  (2)

$$HOC1 + H_2O \stackrel{?}{\leftarrow} H_3O^+ + OC1^-$$
 (2)

The equilibrium concentrations of the various chlorine species are pH dependent. However, there is not significant quantity of  $\operatorname{Cl}_2$  present unless the solution is strongly acidic (pH <3.0). At pH 4.0 - 5.0 the major species present is the undissociated hypochlorous acid - HOCl, and above pH 7.0 the free hypochlorite ion is present in significant quantities (44).

The chlorination of waters usually takes place at pH levels under which HOCl and OCl are the dominant species present and hence these

will determine the types of organohalides formed by reactions with organic compounds initially present in the water. Therefore, free radical type reactions involving chlorine atoms are not expected to be important. Electrophilic substitution and addition reactions are the major mechanisms leading to the formation of organohalides. HOCl and OCl are powerful oxidizing agents and it is oxidation that almost entirely accounts for the chlorine demand in both natural and sewage water treatment (45).

In 1974, Rook (46) published a paper describing the formation of all four haloforms contianing bromine and/or chlorine during the chlorination of water from the Rhine and Meuse Rivers. During the same year this finding was confirmed by Bellar et al, (47) (with the exception of bromoform), in a number of U.S. municipal waters which had been subjected to chlorination treatment. Since then, several studies have confirmed that a number of organohalides are formed in varying concentrations during chlorination treatment (see Section 12.4.4).

The mechanism of organohalide formation and the organic precursors may vary depending on the organic composition of the water being treated.

Reaction pathways are not well understood.

Rook, 1974 (46) reported experimental evidence that in the chlorination treatment of natural waters the formation of haloforms results as a by-product of reactions involving naturally occurring fulvicacids.

Fulvic acids are a subgroup of humic acids. According to Dragunov, 1961 (48) and Kleinhempel, 1970 (49) humic acids consist of polymers of polyhydroxybenzenes, polyhydroxybenzoic acids, benzene polycarboxylic

acids, sugars, and small amounts of N-bases. Humic and fulvic acids both give identical monomeric by-products in various degradation methods surveyed by Schnitzer and Khan, 1972 (50).

In an investigation of the reactive pathways leading to the formation of organohalides during chlorination of waters containing fulvic and humic acids, Rook, 1977 (51) speculated that hydroxylated aromatic rings with two free meta-positioned OH-groups may be available active sites for haloform formation. This contention was supported by a study of organohalide formation using as model precursors smaller natural glycosides containing the proposed active sites.

In a recent study reported by Looyenga et al, 1977 (52) a drinking water treatment plant in Huron, South Dakota was studied to determine where halocarbons were formed during the treatment process.

Samples were analysed from the raw water intake, point of lime addition (prechlorination is usually also carried out here), at post clarification, post filtration and at the clear well. It was found that haloforms appeared at the point of lime and chlorine addition where the pH is high (11 to 12). If the pH is reduced to 7 before chlorine is added the yield of organohalides is reduced. They also found that the concentration of haloforms increased with time along the distribution system.

They point out that there are practical problems associated with control of pH to 7 or lower and that even with control the potential chloroform concentration in the water was high with concentrations rising to 200-350 ppb within the distribution system.



In a study carried out by the Ontario Ministry of the Environment, Nicholson et al, 1976 (53) report a difference in observed haloform concentrations using gas sparging and direct aqueous injection techniques with gas chromatography. They conclude from their study that, when using the direct aqueous injection technique, compounds which are precursors of haloforms react at high injector temperatures to produce haloforms. Thus the direct aqueous injection technique is interpreted as giving a value which is a measure of the maximum haloform concentration which can be reached in the distribution system. This was called the total potential haloform concentration while the value from gas sparging methods is referred to as the free haloform concentration.

# 12.4.2 AQUEOUS TRANSPORT AND TRANSFORMATION

Organic compounds, once present in a water course, are subject to transport along the water body, dilution by turbulent mixing, chemical and physical transformations, biological degradation and removal by adsorption on the bottom sediment or on suspended particles and by evaporation.

Many compounds, especially those of low solubility and high vapor pressure, can readily be evaporated from one location, advected in an air mass to a new location, and redissolved in another water body.

Mackay et al, 1973 (54), using thermodynamic considerations, calculated evaporative half lives for a number of organic compounds from water bodies. Using activity coefficients, the equilibrium vapor

composition of a water-hydrocarbon mixture above the water surface can be determined. The following assumptions are made:

- the organic compound is in true solution and not in suspended, colloidal, ionic, complexed or adsorbed form
- the vapor formed is in equilibrium with the liquid at the interface
- mixing in the water is sufficiently fast that the concentration at the surface is close to that of the bulk of the water
- the water evaporation rate is negligibly affected by the presence of the organic compound

Half lives calculated in this manner ranged from 15 min. to 3 hours.

In situations where the water body is turbulent with frequent exchange between the surface water layer and the bulk, (for example in a fast-flowing shallow river or during white capping on a lake) the assumption of rapid mixing between the surface and the bulk of the water may be quite good. However, for other situations the observed evaporation rates may be lower than calculated evaporative half lives due to liquid diffusion limited conditions. In a later report Mackay et al, 1975 (55), modified their earlier calculations on evaporative half lives to allow for partial liquid phase diffusion control. Use was made of mass transfer rates in water bodies as suggested by Liss et al, 1974 (56). This resulted in longer half lives of about 5.0 to 7 hours.

Dilling et al, 1975 (57) report a study of evaporation rates of methylene chloride, chloroform, l,l,l-trichloroethane, trichloroethylene,



tetrachloroethylene, and other chlorinated compounds from water at the 1 ppm level and below. Calculations based on the work of Mackay et al, 1973 (54) were carried out to predict evaporation half lives and these were compared with experimental values.

The results of experimental and calculated evaporation times from a slowly stirred open container are shown in Table 12-11. With the exception of tetrachloroethane, which had an average half life of 50 min., all of the compounds listed had similar short half lives in solution with an average of 23 min. The stirring speed was reported to have a marked effect on evaporation rates. With stirring for 15 sec. every 5 min. the average half life for evaporation was greater than 90 min.

Calculated evaporation half lives are much lower than experimental.

This is likely due to the nonuniform concentrations in solution resulting from depletion of the solute near the surface of the water.

This would lead to a partially aqueous diffusion limited evaporation rate.

It was also found that addition of other solutes such as sodium chloride or propylene glycol, or sedimentary material such as bentonite clay, had little effect on the observed evaporation half lives.

If aqueous chemical or biological degradation paths are to be significant then the half lives for these processes must be such that they can compete with the processes of evaporation and atmospheric degradation.

Pearson et al, 1975 (37) report that aqueous degradation (in the absence of actinic light) of aliphatic organochlorine follows first order kinetics with respect to the concentration of the organochlorine.

# EVAPORATION RATES OF CHLORINATED COMPOUNDS

# FROM DILUTE AQUEOUS SOLUTIONS

		EVAPORATION TIME	(min.) Calculated
COMPOUND	50%	90%	50%
Methyl chloride	27	91	_ = _
Methylene chloride	21	69	2.3
Chloroform	21	71	1.4
Carbon tetrachloride	29	97	
Chloroethane	21	79	
l,l-dichloroethane	22	109	
1,2-dichloroethane	29	96	
Methylchloroform	23	69	0.34
1,1,2-trichloroethane	21	102	
1,1,1,2-tetrachloroethane	43	>120	
1,1,2,2-tetrachloroethane	56	>120	
Vinylidene chloride	22	89	
1,2-dichloroethylene (cis)	18	64	
1,2-dichloroethylene (trans)	24	83	-
Trichloroethylene	21	69	0.48
Perchloroethylene	26	83	0.56

The half lives of tri- and perchloroethylene were estimated to be 2.5 and 6 years respectively. Paraffinic organochlorines, such as tetrachloroethane, more readily undergo dehydrochlorination in reactions which are pH dependent. At 15 °C and a pH of 7 sym-tetrachloroethane has a half life of 2 years, while the half life falls to 26 days at a pH of 7.7. These aqueous degradation reactions are considerably accelerated in water in the presence of metals such as iron.

In another study Dilling et al, 1975 (57) report an experimental study on the decomposition rates of chlorinated compounds in aerated water in the dark and in sunlight. Methylene chloride, chloroform, methyl chloroform, and tri- and perchloroethylene were studied. Half lives range from 6 to 18 months and were not strongly affected by sunlight (Table 12-12). Although the data of Pearson and Dilling do not agree they both indicate aqueous chemical reaction half lives which are much longer than expected evaporation half lives. In the case of Dilling's experiments it is possible that part of the observed reactions occurred in the vapor phase in the small air space above the solution sealed in their quartz tubes.

Biochemical degradation of chlorinated hydrocarbons is generally thought to be very slow. Pearson et al, 1975 (57) were unable to detect any significant oxygen absorption from compounds containing only C, H and Cl. Lu et al, 1975 (58) report a study on chlorobenzene in which its biodegradability index was found to be similar to DDT.

TABLE 12-12

DECOMPOSITION RATES OF CHLORINATED COMPOUNDS IN

AERATED WATER IN THE DARK AND IN PRESENCE OF SUNLIGHT

	0 m Dark	onth Light		onth Light		onth Light	Dark Reaction 1/2 month
Methylene chloride	1.00	1.00	0.76	0.79	0.68	0.64	∿18
Chloroform	1.00	1.00	0.73	0.75	0.63	0.56	∿15
Methyl chloroform	1.00	1.00	0.46	0.46	0.26	0.32	6
Trichloroethylene	1.00	1.00	0.68	0.56	0.44	0.21	10.7
Perchloroethylene	1.00	1.00	0.63	0.52	0.35	0.24	8.8

# 12.4.3 MEASURED CONCENTRATIONS IN NATURAL WATERS AND EFFLUENTS

Most of the available literature dealing with the quantification of light chlorinated hydrocarbons in water is concerned with drinking water supplies. These compounds can, however, also be found in industrial effluents, rivers, lakes and other water bodies. In fact, studies indicate that chlorinated  $C_1$  and  $C_2$  hydrocarbons such as trichloroethylene, perchloroethylene, trichloroethane, carbon tetrachloride, and chloroform are ubiquitous in the aqueous environment at trace levels, Pearson et al, 1975 (37).

In a recent European study carried out by producers of chlorinated solvents in western Europe, (Correia et al, 1977 (35)), analysis of river, canal and sea waters for trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane are reported (Table 12-13). The sites sampled include those receiving effluents from producers and users of chlorinated hydrocarbons. Concentrations found are generally in the ppb range but are highly variable.

In a study of naturally occurring halocarbons in air and the sea, Lovelock, 1975 (59), reports finding relatively high levels of methyl chloride in the sea off the coast of England near Dorset. Concentrations found vary from 6 to 21 ppb. These high concentrations are attributed to the conversion of methyl iodide (present in significant concentrations as a result of biological production from kelp beds in the area) to methyl chloride in sea water.

# CONCENTRATIONS OF CHLORINATED HYDROCARBONS

# IN WESTERN EUROPE

# CONCENTRATIONS (ppb)

LOCATION		COUNTRY	TRICHLORO- ETHYLENE	TETRACHLORO- ETHYLENE	1,1,1-TRI CHLOROETHANE
Liverpool Bay		U.K.	0.3-3.6	0.12-2.6	<0.25-<3.3
River Rhine	Hoenningen Leulsdorf Wesseling	<b>D</b>	1-1.5 2-2.5 1.5-2	1.5 2-2.5 1.75	
River Salzach	Marienberg Uberackern		0.4-2.1 25-73.9	0.6-1.9 3.3-19.6	
River Isar	Source of river Munich Downstream of Munich Lake Starnberg Lake Lerchenau		0.02-0.03 0.2-0.6 2.5-3.2 0.13-0.15 3.2-8.5	0.01-0.02 0.1-1.0 1.9-2.5 0.15-0.20 2.0-2.8	
Twente Canal H Twente Canal D Eems Oostfriese Gaa Oostfriese Gaa Ranselgat Huibertgat	engelo elden tje (South)	NL	0.26 <0.2 11.0 7.5 0.7 0.2 <0.2	0.3 <0.2 16.0 6.6 1.4 1.7	0.07 <0.1 <0.1 0.3 0.1 0.3 0.2
River Duranee	Point Oraison Ste Tulle	F	6-25 <3-9	<10-46 <5	N D N D

ND Not detected.



Pearson et al, 1975 (37) and McConnell, 1976 (45) have reported the results of extensive studies of fresh waters, sea water, marine sediments and other media for the presence of chlorinated  $\rm C_1$  and  $\rm C_2$  hydrocarbons in England (Table 12-14). It is significant to note that no organochlorines were detected in well water samples. Vinylidene chloride was not detected in any of the natural water samples analysed.

From their data it is concluded that the chlorinated C  $_{\rm l}$  and C  $_{\rm 2}$  hydrocarbons do not accumulate in marine sediments.

In a recent study of a specialty chemicals manufacturing plant,

Jungclaus et al, 1978 (60) report the results of analyses of waste water

effluents, river water and river sediments in the vicinity of the plant

for a wide range of organic compounds.

With the exception of a few chlorinated hydrocarbons (eg methylene chloride in waste water which was reported present at concentrations of 3-8 ppm) most of the organohalides were not quantified. Chlorinated hydrocarbons found to be present in the plant's effluent stream include: methylene chloride, chloroform, trichloroethane, trichloroethylene, tetrachloroethylene, chlorobenzene, and dichlorobenzene. With the exception of chloroform and trichloroethane, all of these compounds above were also found in river water samples. No detectable amounts of these compounds were found to accumulate in the river sediments.

In late 1974 and 1975, the Ontario Ministry of the Environment initiated an investigation into organics in industrial effluents and sediment along the St. Clair River in the Sarnia area. Preliminary results have been reported (61).

# IN ENGLAND (ppb)

A) AVERAGE CONCENTRATIONS IN RAIN WATER AND UPLAND WATERS OF THE CLYWEDOG AND RHAEDR RIVERS IN WALES

COMPOUND	CONCENTRATION
Chloroform	0.2
Carbon Tetrachloride	0.3
Trichloroethylene	0.2
Perchloroethylene	0.2
1,1,1-Trichloroethane	0.1

B) AVERAGE CONCENTRATIONS IN MUNICIPAL WATERS FOR LIVERPOOL, MANCHESTER AND CHESTER

COMPOUND	CONCENTRATION
Chloroform	2.0
Carbon Tetrachloride	0.3
Trichloroethylene	6.0
Perch loroethy lene	0.4
I, I, I-Trichloroethane	0.3

C) AVERAGE CONCENTRATIONS IN LIVERPOOL BAY SEA WATER

COMPOUND	CONCENTRATION
Chloroform	1.0*
Carbon Tetrachloride	0.25
Trichloroethylene	0.3
Perchloroethylene	0.12
l, l, l-Trichloroethane	0.25

<sup>\*</sup> maximum, too few samples for average

A total 26 sites (mainly industrial outfalls) were sampled. There were 47 organic compounds identified of which 21 were organohalides. Since all of the analyses were performed on grab samples the results cannot be considered as representative of the average concentrations of compounds in the effluents as most of the industrial processes do not operate in a steady state and rapid fluctuations in discharges can be expected.

Six of the organohalides in plant effluents were determined quantitatively including chloroform, trichloroethylene, and carbon tetrachloride (Table 12-15). Concentrations found were highly variable. Carbon tetrachloride was found in the ppm concentration level at three sites while chloroform reached close to 1 ppm at one site. Other chlorinated compounds of interest identified at the 10 to 100 ppb concentration level are found on Table 12-16.

Sediment samples showed the presence of only the heavier chlorinated organics with the exception of one site (Table 12-17). It is concluded that the chlorinated  $C_1$  and  $C_2$  hydrocarbons do not accumulate in the St. Clair River sediments (62).

#### 12.4.4 MEASURED CONCENTRATIONS IN DRINKING WATERS

As a result of advances in available analytical techniques a large amount of data has accumulated on the levels of trace organics in waters over the past five years. The problem of organic contamination of drinking water has become the subject of considerable concern and debate.

TABLE 12-15

# QUANTITATIVE ANALYSIS OF VOLATILE ORGANOHALIDES

# IN PLANT EFFLUENTS

EFFLUENT	ORGANOHALIDES (ppb)					
	Vinyl chloride	Chloroform	Dichloro- bromomethane	Dibromo- chloromethane	Trichloro- ethylene	Carbon- tetrachloride
C-1	1	-	-		102	110
C-2	-	6	-	-	-	20
C-3	<b>:</b>	13	-	-	4	12
C – 4	4	912	150	66	-	1390
C-5	-	70	21	-	-	13
c-6	13	-	#	-	-	1378
C-7		5	-		-	15
c-8	-	-	-	-	-	100
C-9	-	> <del>-</del>	-	-	-	16
C-10	-	5	-	NEG.	-	12
C-11	-	5 <del>,00</del> 1		-	-	67
F-2	32	-	-	-	2	-
1-2	-	: <del></del>	-	( <del></del>	·	91
1-8	11	-	-	_	_	12
K-1	172	-	-	-	-	±
K-2	30	55	-	-	-	-
K-3	4	_	-	-	-	-
K-4	384	-	-	-	-	•••
K-5	1	=	-	-	-	¥
к-6	215	2		-	18	Ψ,
K-7	10	-	-	-	-	-
M- 1	+	-	-	_	÷	19
M~2	-	202	-	-	-	981
Detection						
Limits *	1.0	1.0	0.5	1.0	2.0	1.0
*ua /1				7		

# LEVELS OF VARIOUS HYDROCARBONS AND ORGANOHALIDES

# IN PLANT EFFLUENTS

+ = identified at 10-100 ug/l levels -= i

- = none detected (less than 10 ug/1)

EFFLUENT	Butadiene	Diethylbenzene	Dimethyl- diethylbenzene	Diphenyl ether	Chloroethane	Dichloroethanes	Trichloroethane	Tetrachloroethane	Tetrachloro- ethylene	Dichloro- propane	Tetrachloro- propane	Hexachloro- butadiene
C-1		+	<u> </u>	*		+		•	+	*		_
C-2	_					+	•	•	4		*	
C-3		+	-	-	-	+	_	-	+	+		_
C-4	-	-	•	-	-	+	_	_	+	-	-	
C-5	-	-	-	-	-	-	-	+	+	+	+	4
C-6	-	+	-	+	-	-	+		_		_	
C-7		1. <del>***</del> /2	. +	-	-	*	-	-	-	-		-
C-8	-	+	+	+	-	+	_	-	+	_	-	-
c-9	-	-	-	••	-	+	-	-	+	-	_	
C-10	-	+	+	_	9 <b>9</b> 0	+	-	-	+	-	-	_
C-11	•	-	-	-	-	+		-	+	-	-	-
F-2	-	-	-	-	•	+	+				_	+
1-2	±.	-	-	-	-	-	-	*		-	-	-
1-8	-	-	-	-	•	-	-	-	-	-	-	-
K-1	-	•	-	-	-	-	-	*		-	-	-
K-2	-	-	•	-	l <del>-</del>	7	-	-	-	-	-	-
К-3 К-4	-	-	-	-	-	-	-	-	-	-	-	•
	+	-	-	-	-	-	*	-	-	-	-	-
K-5 K-6	-	-	-	•	+	-	-	-	-	-	-	•
	-	-	*	-	+	+	-	+	-	-	-	+
K-7 M-1	-	-	-	-	•	-		+		-	-	-
M-2	-	-	7	-	-	•	-	-	***	-		-
	-		-	-	-		-	-	-	-	-	-

# ORGANIC COMPOUNDS IDENTIFIED IN

# ST. CLAIR RIVER SEDIMENTS

LOCATION	COMPOUNDS IDENTIFIED	CONCENTRATION (ppm)
SA-1	Dichlorobenzene	=
SA-2	Tetrachlorobutadiene	*
	Dimethylnaphthalene	-
SB-1	Tetrachloroethylene	-
	Hexachloroethane	-
	Pentachlorobutadiene	-
	Hexachlorobutadiene	-
	Dichlorobenzene	-
	Trichlorobenzene	-
SB-3	Tetrachloroethylene	-
	Hexachlorobutadiene	-
	Diethylbenzene	-
	Bromochlorobenzene	-
SB-4	Chloroform	-
	Carbon tetrachloride	200
	Trichloroethylene	100
	Tetrachloroethylene	400
	Hexachloroethane	-
	Hexachlorobutadiene	50
SE	Alkanes	-
SH	None	_
SI	None	-
SJ	Alkanes	-



In November 1974 the U.S. Environmental Defense Fund published a report indicating a possible link between certain cancers and the consumption of Mississippi River water by persons living in Louisiana (63). At the same time the US-EPA released a draft report (64) identifying the presence of a number of organic compounds, some of them suspected carcinogens, in the New Orleans water supply. The final copy of this report identified a total of sixty-six organic compounds (65). These reports led to the easy passage of the U.S. Safe Drinking Water Act in November, 1974.

As a result of this legislation the US-EPA expanded the New Orleans study to a National Organics Reconnaissance Study involving 80 cities during 1974 and 1975 (66).

It was decided to determine the presence of six organic compounds of particular concern: chloroform, carbon tetrachloride, 1,2-dichloroethane, bromodichloromethane, dibromochloromethane, and bromoform.

None of the raw, or untreated, waters sampled contained dibromomethane or bromoform, and only 62 % contained any chloroform or bromodichloromethane. Of these, 58.4 % contained very small concentrations of chloroform (0.1 to 0.9 ppb) while the other 3.6 % contained no chloroform but had low concentrations of bromodichloromethane, 1,2-dichloroethane, and/or carbon tetrachloride in various combinations.

In contrast to these findings for raw water, it was found that at all locations the finished or treated water contained chloroform in concentrations ranging from less than 0.1 to 311 ppb with 50 % containing 25 ppb or less. Only very small amounts of 1,2-dichloroethane and carbon

tetrachloride were found in the finished waters. Of the supplies that contained 1,2-dichloroethane, 32.9 % of the total, 6 ppb was the highest concentration found; of the 12.6 % having carbon tetrachloride, the highest level was 3 ppb. Table 12-18 summarizes the results for raw and finished waters.

Five cities were chosen for a more comprehensive study. The results identified 85 organic compounds present in finished waters of one or more of the cities. These include:

methyl chloride 1,1,2-trichloroethane methylene chloride 1,1-dichloroethylene chloroform trichloroethylene carbon tetrachloride perchloroethylene chloroethane ch lorobenzene o-dichlorobenzene l, l-dichloroethane 1,2-dichloroethane m-dichlorobenzene 1,1,1-trichloroethane p-dichlorobenzene

The US-EPA is currently conducting a National Organic Monitoring

Survey for the purpose of obtaining data in support of the possible

establishment of additional maximum contaminant levels of organic

compounds in drinking water. Included are 113 city public water supplies

which are being variously monitored for some 20 parameters (62). In all

but two of the cities, chloroform was found to be present as well as a

number of other compounds (see Table 12-19). This study is still in

progress.

# WATER ANALYSIS FROM U.S. NATIONAL ORGANIC

#### RECONNAISSANCE SURVEY

#### A) RAW WATER ANALYSIS

	C OMPOUND	NUMBER OF LOCATIONS DETECTED	RANGE OF CONCENTRATIONS (µg/liter)
	None Detected Chloroform Bromodichloromethane Dibromochloromethane Bromoform 1,2-dichloroethane Carbon Tetrachloride	30 45 6 0 0	- <0.1 - 0.9* <0.2 - 0.8* - * - <0.2 - 3 <2 - 4
в)	FINISHED WATER ANALYSIS		
	Chloroform Bromodichloromethane Dibromochloromethane Bromform Carbon Tetrachloride 1,2-dichloroethane	79 76 70 25 10 26	0.1 - 311 1.8 - 116 0.4 - 100 1.0 - 92 2.0 - 3 0.2 - 6

<sup>\*</sup> One additional location received raw water prechlorinated by a nearby industry. This water contained 16  $\mu g/l$  of chloroform, 11  $\mu g/l$  bromodichloromethane, and 3  $\mu g/l$  dibromochloromethane.

# US NATIONAL ORGANIC MONITORING SURVEY

# OF DRINKING WATER SUPPLIES

COMPOUND	FREQUENCY OBSERVED (%)	AVERAGE CONCENTRATION FOR POSITIVE RESULTS (ppb)
Methylene Chloride	14	6.1
Chloroform	95	62.0
Carbon Tetrachloride	8	4.0
Ethylene Dichloride	2	1.4
Trichloroethylene	14	4.2
Perchloroethylene	20	1.0
Dichlorobenzene ortho- meta- para-	2 1 15	2.5 0.1 0.7

Even before these American studies, Novak et al, 1973 (67) reported finding at least fifteen compounds in drinking water ranging from 0.1 to 6 ppb. Included among the compounds identified were chloroform, carbon tetrachloride, perchloroethylene, and dichloroethane. Rook, 1972 (68), in a study of treated water obtained from the Rhine River reported finding a number of organic compounds including:

chloroform perchloroethylene
carbon tetrachloride chlorobenzene
dichloroethane
trichloroethylene

Grob, 1973 (69) reported the identification of 50 organic compounds in Zurich tap water. Included among these was dichlorobenzene. McConnell, 1976 (45) has reported the presence of chloro-bromo-haloforms present in municipal drinking water in England (Table 12-20).

Rook, 1974 (46) reported that chloro and/or bromo haloforms were major contaminants of drinking water from the Rhine and Meuse Rivers and, furthermore, these haloforms are introduced or formed during the water treatment process, and were not generally present to the same extent in raw water supplies. Bellar et al, 1974 (47) confirmed the conclusions of Rook (bromoform excepted) in a number of US municipal waters which had been subjected to chlorination.

During 1974 the Ontario Ministry of the Environment initiated an extensive study of volatile organic compounds in Ontario drinking waters prompted by the increasing number of reports of organohalides in drinking water.

TABLE 12-20

HALOFORMS IN N.W. ENGLAND MUNICIPAL WATERS (ppb)

	CHC13	CHC1 <sub>2</sub> Br	CHC1Br <sub>2</sub>	CHBr <sub>3</sub>
Hale, Manchester	20-35	11-27	0.01-3	<0.01
Saughall, Wirral	17-38	11-20	1.5-2.2	<0.01
Aigburth and Woolton, Liverpool	7-15	3-10	0.3-1.1	<0.01
Widnes, Cheshire	1- 7	1- 3	2 -3	<0.1-2.5
Sandiway, Cheshire	0.7-5	1- 2	1 -2	0.7-2

A total of 48 water treatment plants were sampled and analysed. Raw water sources were also sampled. The results were reported by Smillie et al, 1977 (70) and are summarized in Table 12-21, 12-22 and 12-23. Chloroform, carbon tetrachloride, perchloroethylene, dichlorobromomethane and chlorodibromomethane concentrations were determined.

In general carbon tetrachloride was either not detected or present in only trace quantities. The same was found for perchloroethylene.

Dichlorobromomethane and chlorodibromomethane were found in concentrations ranging from not detectable to around 20 ppb. Dichlorobromomethane was usually found in higher concentrations than chlorodibromomethane.

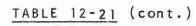
Chloroform was often the predominant organohalide found and ranged from 1 ppb or less up to 159 ppb.

Generally chloroform levels varied with different raw water sources. Ground-water generated the lowest concentrations of chloroform in finished water. The Great Lakes, which serve about 65 % of Ontario's population with drinking water, generated a relatively low level of chloroform while rivers and lakes had the highest (71).

# UNITED TECHNOLOGY and SCIENCE INC.

TABLE 12-21 AVERAGE VOLATILE ORGANOHALIDE CONCENTRATION IN µg/1

	NUMBER OF	CHC13	CC14	<sup>C</sup> 2 <sup>HC1</sup> 3	CHC1 <sub>2</sub> Br	CHBr <sub>2</sub> C1
LOCATION*	DETERMINATIONS	Conc., (σ %)	Conc., (0 %)	Conc., (σ %)	Conc., (σ %)	Conc., (σ %)
Acton (W)	1	1	nd	nd	nd	nd
Amherstburg (GL-E)	8	60, (37)	nd	nd	19, (29)	3, (77)
Belleville (R)	12	140, (41)	T	T	13, (32)	nd
Blenheim (GL-E)	8	28, (29)	T	nd	9, (30)	2, (31)
Bowmanville (GL-0)	9	27, (66)	T	T	12, (34)	4, (59)
Brantford (R)	31	159, (30)	T	T	22, (55)	Ť
Burlington (GL-0)	5	19, (60)	T	nd	9, (13)	4, (0)
Cayuga (R)	25	117, (53)	T	T	20, (50)	nd
Chatham (R)	5	23, (54)	nd	nd	12, (64)	4, (55)
Dresden (R)	3	111, (27)	nd	nd	13, (39)	T
Elgin (GL-H)	11	47, (29)	T	nd	14, (58)	5, (44)
Georgetown (W)	1	6	nd	nd	nd	nd
Goderich (GL-H)	8	44, (48)	T	nd	9, (59)	3, (165)
Grand Bend (GL-H)	6	27, (35)	T	T	8, (43)	3, (45)
Guelph (W)	1	nd	nd	nď	nd	nd
Halton (W)	1	11	0.7	nd	8	3
Harrow-						
Colchester (GL-E)	12	75, (34)	.5, (147)	3, (170)	17, (36)	4, (44)
Hawkesbury (R)	2	43, (25)	nd	2	2	nd
Kingston (GL-0)	5	37, (34)	.2, (117)	T	14, (20)	4, (61)
Markham (W)						
Don Mills WTP	2	3	nd	nd	5	13
John St. WTP	1	36	nd	nd	41	38
Napanee (R)	6	74, (58)	.4, (175)	nd	9, (35)	nd
Newcastle (GL-0)	2	20	3	T	13	6





UNITED TECHNOLOGY and SCIENCE INC.

LOCATION*	NUMBER OF DETERMINATIONS	CHC1 <sub>3</sub> Conc., (σ %)	CC1 <sub>4</sub> Conc., (σ %)	C <sub>2</sub> HC1 <sub>3</sub> Conc., (σ %)	CHCl <sub>2</sub> Br Conc., (σ %)	CHBr <sub>2</sub> Cl Conc., (o %)
Niagara-on-the-Lake (GL-0) Oakville (GL-0) Ottawa (R)	2 6	28 18, (26)	nd .3, (217)	nd T	16 11, (14)	4 5, (13)
Britainnia WTP Lemieux WTP Pembroke (R) Port Lambton (GL-H) Prescott, GL-O) Renfrew (R) Sarnia (GL-H) Sault Ste. Marie	3 2 4 8 3 3	55, (143) 56, (126) 65, (45) 23, (52) 25, (34) 52, (42) 38	.3, (173) nd nd T nd 6	nd nd nd nd nd nd	nd 2, (141) 1, (141) 8, (36) 8, (130) 1	nd nd 3, (31) 1 nd 5
(GL-S) Smith Falls (R) Sombra (GL-H) Southampton (GL-H) Sudbury Coniston WTP (L) Lake Ramsey WTP (L)	3 7 2 3 5 ) 5	11, (9) 42, (24) 38 47, (40) 116, (33) 42, (29)	nd .5, (90) 6 .7, (166) .8, (202) .3, (171)	nd nd nd nd nd	nd 2, (74) 9 11, (19) 5, (64) 6, (79)	nd nd 5 3, (65)
Thunder Bay Bare Pt. (GL-S) Loch Lomond WTP (R) Toronto (GL-0)	17	33, (30) 76	T nd	nd nd	7, (76) 17	2, (79) T 18
Lakeview WTP R.C. Harris WTP Westerly WTP Trenton (R) Union (GL-E) Whitchurch-	5 8 5 13 9	6, (42) 8, (76) 8, (25) 145, (26) 41, (45)	nd T T T	nd T T T nd	6, (46) 5, (97) 5, (14) 9, (38) 14, (31)	1 2, (83) 4, (113) T 3, (46)
Stouffville (W) Windsor (GL-H)	1 9	60 38, (46)	rid T	nd nd	8 14, (54)	4 3, (84)

## TABLE 12-21 (cont.)

\* Raw water sources

GL - Great Lakes System

S - Superior

H - Huron

E - Erie

0 - Ontario

R " River

W - Well

L - Lake

 $\sigma\%$  -  $\sigma\%$  Relative standard deviation

nd - not detected

T - trace

TABLE 12-22

# AVERAGE TOTAL HALOFORM CONCENTRATIONS

# FOR VARIOUS RAW WATER SOURCES

Source	CHCl <sub>3</sub> Concentration (pg/l)			CHCl <sub>2</sub> Br Concentration (µg/l)		
n = no. sites	Average	Low	High	Average	Low	High
Rivers (n = 14)	82	23	159	9	nd	22
Lakes * (n = 2)	79	42	116	55	4	7
Great Lakes System (n = 23)	31	6	75	10	nd	19
Wells (n = 7)	17	nd	60	8.9	nd	41

<sup>\* 2</sup> locations in Sudbury

TABLE 12-23

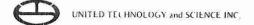
# AVERAGE TOTAL HALOFORM CONCENTRATIONS FOR FINISHED WATER WITH GREAT LAKES SOURCES

Creat Lakes	No. of Sites	CHCl <sub>3</sub> Average Concentration µg/l, ( $\sigma$ %)*	CHCl <sub>2</sub> Br Average Concentration $\mu g/1$ , $(\sigma %)$
Superior	2	22, (71)	3.5, (141)
Huron	8	36, (29)	10, (26)
Erie	4	51, (41)	15, (29)
Ontario	9	20, (51)	10, (39)

<sup>\*</sup> Relative standard deviation

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### 13.1 INTRODUCTION

The data in this section are drawn from a variety of sources such as animal studies, short term human experiments, accidents, and experience derived from occupational exposures. Very seldom is there information derived from situations which duplicate life time community exposures. Therefore, almost all judgements about the actual or potential health effects of the compounds in this report when considered as air pollutants involve varying degrees of extrapolation and these in turn must be based on certain assumptions.

An effort has been made to highlight those health concerns which can reasonably be related to the anticipated level of exposure of the general population to the particular pollutant. If the possible health effect is serious, attention has been drawn to it even if the projected level of exposure of the community is well below the level at which the effect has been found. Particularly for agents that have been shown to cause cancer, or are suspected carcinogens, a straight line relationship between dose and effect has been assumed.

There is no entirely satisfactory method of handling the question of the highly variable response to be expected among any group of humans subjected to the same level of pollutant. This matter is usually handled by using a "safety factor" in setting standards but it is generally recognized that this is an arbitrary procedure with little scientific data upon which to base the calculations. It has not been within the terms of reference of these reports to suggest



air quality standards but rather to set out the health data

available at this time that can be used as one input into the standard
setting process.

### Comment on the Summary of Biological Information

### Appended to a Consideration of Each Pollutant

To be useful a summary must be short, but the abbreviations carry with them considerable risks, since by dropping information on experimental conditions, the variability of the effects measured, and a host of other qualifying factors, an appearance of precision and authority is given to the data which is seldom warranted. It is hoped that the rating system will only be used in setting priorities and that it will be constantly reviewed to allow consideration of new data.

Obviously, such a cryptic rating system as that used in this summary of the biological effects of the selected chemicals contains a considerable measure of subjective judgement. By using only three rating categories (A, B, and C), it is hoped that enough information is provided for a simple ranking of chemicals to be undertaken on the basis of their biological actions. This ranking can then be compared with other ordering systems based on such characteristics as production, emission levels, etc.

A further advantage of a very simple system of assigning categories lies in its obvious limitations, which, because they are obvious, may serve as a warning that the data upon which the categories are based are very seldom complete and/or are often not of a uniformly high quality. It is particularly important to bear this caveat in mind

with regard to data derived from human experience, where the investigator must work with the available information which has usually been collected for quite other reasons than those motivating his own study.

Note also that the biological rating system refers only to toxicity which is the ability to cause harm after reaching the target organ of organism. The more important factor upon which to base policy and administrative decisions is related to the <a href="hazard">hazard</a> to health that a chemical poses. Hazard is an experssion of the probability that a chemical will reach the target organ or organism in sufficient quantity to cause harm. Hazard must take into account such factors as the spatial and temporal relationships between the emissions and the receptor, transport factors, numbers of receptors, etc.

Of the three letters used for ranking, A represents the highest toxicity and C the lowest.

### 13.2 METHYL CHLORIDE

### 13.2.1 SUMMARY OF BIOLOGICAL INFORMATION

Central nervous system depressant. No chronic effects reported at occupational exposure limit levels of 100 ppm (TWA) but no systematic studies reported. Mutagenic in the Ames Test. No reports of carcinogenicity in man or animals, but no long term tests conducted.

Toxicity Rating: [B]

Toxicity to Animals

<u>Test</u> <u>Rating</u>

Acute Moderate

Chronic Moderate

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological No Data

### 13.2.2 METABOLISM

Chloromethane (methyl chloride), although less toxic than bromomethane, produces severe neurological disturbances in the animals tested. The mechanism of the toxic effect is not understood but may be related to methylation of SH-groups particularly methylglutathione. Other findings in methyl chloride poisoning are decreases in aldolase activity in the Krebs Cycle and amounts of glutathione in the liver, brain, and kidney. Increases in methyl-glyoxal in the brain due to interference with glutathione metabolism may be the causative factor in the neurological

effects produced by methyl chloride, Redford-Ellis et al, 1971 (1).

The reaction of chloromethane with glutathione not only removes the glutathione but also produces methylglutatione which inhibits glutathione within the cell.

Glutathione possesses several coenzyme functions. It acts as a cofactor in the glyoxalase system which catalyses the conversion of methylglyoxal to lactic acid, while methylglutathione inhibits this enzyme. The symptoms of methyl chloride intoxication have been described as being similar to those seen in cats following intoxication by methylglyoxal (convulsions, initial excitement followed by listlessness, anuria, anorexia, coma and death), Redford-Ellis et al, 1971 (1).

### 13.2.2.1 ABSORPTION

Methyl chloride is readily absorbed through the lungs. Blood levels of methyl chloride remain low even under continuous exposure conditions. These low levels of methylchloride are thought to be associated with the "soaking-up" of the compound by the very large pool of sulfhydryl groups within the body, Von Oettingen, 1964 (2).

The increased excretion of urinary or fecal coproporphyrin III following methyl chloride exposure is probably another expression of interference with glutathione which is known to accelerate the insertion of iron into protoporphyrin and the loss of glutathione activity may reduce the rate of heme formation with the consequent excretion of the coproporphyrin III, Redford-Ellis et al, 1971 (1).

Since methyl chloride boils at minus 23.7 °C oral absorption of the pure material is unlikely. Slight absorption of methyl chloride through the skin has been reported, Davis et al, 1977 (3).

### 13.2.2.2 DISTRIBUTION AND RETENTION

When methyl chloride labelled with carbon 14 is administered to rats relatively more of the labelled carbon is found in proteins, acid soluble constituents and cell sap than with exposure to chloromethanes with greater chlorine content, Reynolds et al, 1967 (4).

### 13.2.2.3 ELIMINATION

Methyl chloride is relatively slowly excreted and its fate on a quantitative basis is not well accounted for. A relatively small amount is excreted in the bile and urine with an unknown but apparently small proportion excreted by the lungs.

### 13.2.3 ANIMAL EXPERIMENTAL STUDIES

Because of the relatively little information available the experimental studies in animals will be dealt with under a single heading rather than in the more extended format used in the other sections.

Mice exposed to 500 parts per million of methyl chloride for 6 hours daily for a week developed convulsions and the cause of death appeared to be associated with hemoglobinuria.

2,000 parts per million of methyl chloride was fatal to Guinea
pigs during the second or third six hour exposure. Dogs were more
susceptible to methyl chloride poisoning showing symptoms of poisoning



following a single six hour exposure of 500 parts per million and dying following two to six exposures at 1,000 parts per million. Monkeys had convulsions following four to seven six hour exposures to methyl chloride at 2,000 parts per million. Rats, rabbits and cats all became sick and died after exposure to 2,000 to 4,000 parts per million for six hours a day with the rats dying at the end of the third to fifth exposure while the cats died after three to four weeks. Dogs and monkeys appeared particularly susceptible to methyl chloride. Among four dogs exposed to 500 parts per million six hours daily, six days a week, one died after two weeks, one after three weeks and one after four weeks. The fourth dog survived 29 weeks of exposure but developed irreversible neuromuscular damage. Two monkeys exposed under the same conditions and concentrations of methyl chloride died after 16 and 17 weeks of exposure. These monkeys showed progressive debility and became unconscious towards the end of the exposure. The threshold for symptoms of methyl chloride poisoning appeared to lie between 300 and 500 parts per million for dogs and monkeys, Smith et al, 1947 (5).

Using the Ames test methyl chloride showed a significant increase in mutations at concentrations of methyl chloride above 0.8 % ranging up to 20.7 %. Bioactivation was not required to detect mutagenesis.

### 13.2.4 HUMAN EXPERIENCE

Because of the relatively limited information regarding the toxic effects of methyl chloride in humans this data will be presented in summary form. 21 fatalities from methyl chloride exposure had been

reported up to 1962 and since that time no further cases have been listed. Most of these poisonings resulted from leaking refrigeration systems and the drop in the number of cases of human poisoning is probably related to the decreased use of methyl chloride as a refrigerant. Prior to 1962 there were at least 241 non-fatal cases of methyl chloride poisoning reported while since that time only a further 34 cases have been added to the literature. In one instance four members of one family were exposed to methyl chloride leaking from a domestic refrigerator. All four members of the family had symptoms of central nervous system intoxication and kidney injury. Three members of the family were jaundiced and had increased bilirubin levels. The kidney damage resolved in two weeks and all four individuals recovered completely, Spevak et al, 1976 (6).

Eight individuals working in a synthetic rubber plant who were exposed to methyl chloride at levels from 25 to over 10,000 parts per million had symptoms including blurring of vision, headache and loss of co-ordination. The severe headaches occurred intermittently for 7-10 days and, in the more severely intoxicated, were accompanied by nausea and vomiting. The vomiting lasted a few hours while the nausea persisted for several days. The exposed workers became depressed and anxious except for one who was euphoric, MacDonald, 1964 (7).

It is of interest that intravenous cysteine has proved to be highly effective as a treatment for bromomethane intoxication and since the mechanism of action of bromomethane is thought to be similar to that of



methyl chloride, namely the methylation of sulfhydryl groups, cysteine may be of value in methyl chloride poisoning. In some persons poisoned by chronic exposure to methyl chloride psychic disturbances have predominated and have resulted in their being sent to psychiatrists, Lehmann et al, 1943 (8).

One of the problems with occupational exposure to methyl chloride is that, unlike many chlorinated hydrocarbons, methyl chloride is not only colorless but almost free from odor and produces no irritation of mucous membranes. These facts combined with a characteristic latent period between the time of exposure and the onset of symptoms also serves to prolong exposures since the victim is unaware of the presence of the gas.

Very little information is available regarding the lowest levels of methyl chloride that produce toxic effects in man but no documented reports have been found where the level has been estimated to be lower than 500 parts per million. No reports suggesting that methyl chloride is carcinogenic in man or animals have been found although the finding that the compound is mutagenic in the Ames test raises the possibility of carcinogenic effects. No reports suggesting that methyl chloride is teratogenic have been made.

### 13.3 METHYLENE CHLORIDE

### 13.3.1 SUMMARY OF BIOLOGICAL INFORMATION

Central nervous system depressant. Metabolism of compound results in formation of carbon monoxide which results in exposure to methylene chloride and carbon monoxide being additive.

Occupational exposure level based on keeping CO level within acceptable limits. Effect unlikely to be important at ambient CO levels.

Additive effect with CO becomes significant at 75 ppm methylene chloride and 10 ppm CO.

Toxicity Rating:

[C]

Toxicity to Animals

Test Rating

Acute Low

Chronic Low

Toxicity to Man

Test Rating

Experimental Moderate

Epidemiological Moderate

### 13.3.2 METABOLISM

Although the chloromethanes have similarities in their metabolism and their mechanism of action, they also have differences, for instance, carbon tetrachloride and chloroform undergo homolytic cleavage forming

2 or 3 radicals each and both these compounds cause lipoperoxidation and necrosis of the liver. Methylene chloride, however, undergoes heterolytic cleavage and has not been reported to cause either lipoperoxidation or liver necrosis, Fowler, 1969 (9), Van Dyke, 1969 (10), Ugazio et al, 1973 (11).

It has been reported that labelled carbon from carbon tetrachloride and chloroform appeared in the amino acid fraction corresponding to methionine, whereas labelled carbon from methylene chloride and methyl chloride was found in the amino acid fraction corresponding to serine, Reynolds, 1967 (4).

Protein fractions have been shown to be able to catalyze the hydrolysis of methylene chloride to formaldehyde, chloride ion and hydrogen ion, Heppel et al, 1948 (12). In workers exposed to methylene chloride, formic acid has been found in the urine, suggesting that formaldehyde is produced during methylene chloride metabolism in man (13). In 1972, it was reported that human exposure to methylene chloride resulted in elevated levels of carboxyhemoglobin in the blood and raised carbon monoxide levels in the breath, Stewart et al, 1972 (14). Since that time, there have been several other reports of elevated carbon monoxide levels in the blood or breath of man and animals during and following methylene chloride exposure.

Studies using Carbon 14-labelled methylene chloride in rats showed that the increased level of carbon monoxide was derived from metabolism of methylene chloride. It was also shown that there was no increase in

the level of urobilinogen, thus there was no increased endogenous formation of carbon monoxide due to enhanced metabolism of hemoglobin. It was also noted that the carbon monoxide produced by methylene chloride exposure has a prolonged half-life compared with ordinary exposure to carbon monoxide, Carlsson et al, 1975 (15). Although there seems no doubt that carbon monoxide is produced by the metabolism of methylene chloride, it has also been shown that methylene chloride combines with methemoglobin and absorbs light in the analytical range for carboxyhemoglobin and this fact may interfere with carboxyhemoglobin measurements determined spectrophotometrically (13). There appears, however, to be no question that carboxyhemoglobin levels are elevated following methylene chloride exposure both in man and in animals. It has been found that treatment with microsomal enzyme-inducing drugs such as Phenobarbital and 3-methylcholanthrene does not alter the amount of carboxyhemoglobin produced after intraperitoneal injection of methylene chloride or after inhalation of methylene chloride, Kubic et al, 1974 (16).

It has been suggested that hydrolytic dehydrochlorination of methylene chloride might lead to the production of formaldehyde which would then undergo oxidation to form formic acid, which in turn would be oxidized to carbon dioxide and water finally being dehydrated to carbon monoxide and water. Such a mechanism would account for most of the presently available research results regarding methylene chloride exposure.

### 13.3.2.1 ABSORPTION

Methylene chloride is readily absorbed from the lungs. For instance, during 30 minute exposures at rest, at 250 and 500 parts per million of

methylene chloride, about 55 % of the inhaled methylene chloride was absorbed, whereas during similar 30 minute periods of exercise at the same concentrations of methylene chloride, the percent absorbed decreased because of the greater ventilation, however, the absolute amount absorbed was increased by 2 to 3-fold, Astrand et al, 1975 (17). Other investigators have reported the percentage of absorption for methylene chloride to vary from 74 % to 50 %, Riley et al, 1966 (18), Di Vincenzo et al, 1972 (19).

Methylene chloride is moderately well absorbed through the intact skin, Steward et al, 1964 (20).

### 13.3.2.2 DISTRIBUTION AND RETENTION

Apart from the information on the absorption of methylene chloride, little other information was found regarding its absolute or percentage distribution within the body.

### 13.3.2.3 ELIMINATION

Serial measurements of the level of methylene chloride in the breath following exposure can be used to extrapolate backwards to the concentration of methylene chloride experienced during the exposure period. Doubling the exposure time does not double the concentration of methylene chloride in the expired breath but doubling the exposure concentration does, Di Vincenzo et al, 1972 (19).

The urniary excretion of methylene chloride has been studied and it was found that in four persons exposed to 100 parts per million for

two hours, and seven persons exposed to 200 parts per million for the same length of time, that an average of 22.6 micrograms of methylene chloride was excreted in 24 hours by the group exposed to 100 parts per million and an average of 81.6 micrograms of methylene chloride was excreted by the group exposed to 200 parts per million, Di Vincenzo et al, 1972 (19). It was found during these experiments that very little methylene chloride enters fat deposits and muscle tissue, resulting in a short half-life of methylene chloride in the blood, which is calculated to be about 40 minutes. When the exposure time was increased from two to four hours, there was no significant influence on the half-life. The practical consequence of this is that employees exposed to low concentrations of methylene chloride vapor are unlikely to show an accumulation of the compound over a period of days. Methylene chloride excretion from the lung shows an eponential decay curve representative of first order kinetics and with regard to methylene chloride excretion, the body behaves as a two-compartment system.

### 13.3.3 ANIMAL EXPERIMENTAL STUDIES

### 13.3.3.1 HEMATOPOIETIC SYSTEM

Apart from the formation of carboxyhemoglobin referred to earlier, no consistent or significant effect on the formed elements of the blood has been reported.

### 13.3.3.2 NERVOUS SYSTEM

Methylene chloride has been used as an anaesthetic agent in humans and the depressant effect on the central nervous system has been



demonstrated in many animal experiments. Dogs and rabbits exposed at 4000 parts per million showed light narcosis after 2 1/2 hours in the case of the dogs and 6 hours in the case of the rabbits. Mice appeared to be more resistant to the effects of methylene chloride, developing light narcosis after two hours of exposure at 10,000 parts per million (13). Dogs exposed to 15,000 and 20,000 parts per million of methylene chloride lost their corneal reflexes after ten to twenty minutes and complete muscular relaxation developed after twenty to twenty-five minutes. At that time, the methylene chloride concentration in the blood was 42 mg/100 millilitres, Von Oettingen et al, 1949 (21).

Studies of central nervous system activity measured by electroencephalography have been reported in animals exposed to methylene chloride vapor.

Exposures were followed by an initial excitement period which in turn was later followed by deep narcosis at concentrations between 25,000 and 28,000 parts per million; electrical activity stopped after 1 1/2 hours while no significant changes were found at concentrations below 5,000 parts per million.

Sleeping behaviour has been studied in rats exposed to 500, 1,000 and 3,000 parts per million methylene chloride. When not exposed, the animals slept about 56 % of the time and 16 % of this time was spent in REM (Random Eye Movement) sleep. During the exposures to methylene chloride, the total amount of time spent sleeping increased and the time between successive REM sleep periods increased in proportion to the concentration of methylene chloride exposure. At concentrations of

500 parts per million of methylene chloride, there was little effect on total sleeping time and REM sleep was almost identical to that in controls (13).

### 13.3.3.3 RENAL SYSTEM

At fatal concentrations of methylene chloride, the kidneys have shown inflammatory changes, hemorrhages and degeneration of the tubules. At lower levels of exposure, no significant effects on the kidney have been reported.

### 13.3.3.4 GASTROINTESTINAL TRACT

No significant effects of methylene chloride on the gastrointestinal tract have been reported.

#### 13.3.3.5 LIVER

Inhalation of methylene chloride can produce histological changes and increased triglyceride concentrations in the livers of exposed animals. In dogs, these changes have been reported in animals exposed to 1,000 parts per million of methylene chloride for up to fifty days or to 5,000 parts per million of the solvent for twenty-three days, Balmer et al, 1976 (22).

In mice exposed to 100 parts per million for periods ranging from two to eight weeks, altered levels of cytochromes P-450, P-420, and b5, fatty infiltration of the liver and vacuolization in the liver cells were found, Haun et al, 1972 (23).

#### 13.3.3.6 CARDIOVASCULAR SYSTEM

No significant effects of methylene chloride on the cardiovascular system have been reported beyond those that might be expected from the increased levels of carboxyhemoglobin.

## 13.3.3.7 RESPIRATORY SYSTEM

At levels of methylene chloride producing narcosis, examination of the lungs reveals edema with focal necrosis and small hemorrhages. At levels of methylene chloride exposure below those producing narcosis, no effects on the respiratory system have been reported.

#### 13.3.3.8 REPRODUCTIVE SYSTEM

No reports of long-term exposures to methylene chloride in which reproduction had been studied have been found. In experiments in which pregnant rats and mice were exposed seven hours daily to methylene chloride at 1,250 parts per million on days 5 through 15 of gestation, there was an increase in maternal liver weight in both species and extra sternebrae were found in 50 % of the litters of mice from exposed mothers and in 14 % of control litters. Cleft palate and rotated kidneys were each found in two experimental litters and in none of the control litters, Schwetz et al, 1975 (24).

#### 13.3.3.9 ENDOCRINE SYSTEM

No reports of effects of methylene chloride on the endocrine system have been found.

## 13.3.3.10 EYES AND OTHER SENSE ORGANS

Exposure of a variety of mammals to 17,000 mg/cu. meter of methylene chloride for seven hours a day, five days a week, for up to six months, produced no microscopic changes in the appearance of the eye. However, small, transient increases in corneal thickness and intra-ocular tension were found following ten-minute exposures to 1,750 mg/cu. meter of methylene chloride and inflammation of the conjunctiva and eyelids followed contamination of the eye with liquid methylene chloride. In the case of exposure to the vapor, both corneal thickness and intra-ocular tension returned to normal in two days, Ballantyne et al, 1976 (25).

## 13.3.3.11 CARCINOGENICITY

No lifetime exposure studies of methylene chloride in animals have been found, the longest study being ninety days of continuous exposure.

There is no evidence of carcinogenicity in the animal data presently available.

#### 13.3.3.12 MUTAGENICITY

No reports of mutagenic activity of methylene chloride have been found.

#### 13.3.3.13 TERATOGENICITY

Apart from the study reported under Section 13.3.3.8, no other studies of the teratogenicity of methylene chloride have been found.

## 13.3.3.14 FACTORS AFFECTING TOXICITY

When ethyl alcohol is injected intraperitoneally into rats, higher blood alcohol levels were found when the animals were exposed for four hours to 4,200 parts per million of methylene chloride than when they were not so exposed, Kassabart et al, 1974 (26)., Barmer et al, 1976 (22).

Reference has already been made to the additive effect of carbon monoxide exposure and methylene chloride exposure due to the formation of carboxyhemoglobin on exposure to these compounds singly or together.

#### 13.3.4 HUMAN EXPERIENCE

## 13.3.4.1 EPIDEMIOLOGICAL & CLINICAL STUDIES

In the first report in the English language of the toxic effects of methylene chloride, a manufacturer of lacquors, who discontinued the use of methylene chloride because of its effect on the workers, described the effects as: "It dopes them, makes them stupid, they suffer from headaches, are unreliable at their work, and are awfully apt to stumble and hurt themselves, are irritable, unhappy and require constant supervision if they are to be kept from making silly mistakes", (13).

There are a number of reports in the literature of exposures to high levels of methylene chloride, usually as a result of using this compound in a paint remover in a confined space. The complaints are usually of faintness, giddiness and stupor with rapid improvement after the exposure has ended. In persons experiencing very high concentrations

of methylene chloride, pulmonary edema has been found.

The possibility of pulmonary edema occurring following methylene chloride exposure is more likely if the exposure takes place in the presence of open flames or very hot surfaces. This is due to the formation of phosgene as a result of the decomposition of methylene chloride by heat.

In a study of 17 women and 16 men exposed to methylene chloride in the production of cellulose acetate film, the exposed workers reported experiencing a sweet taste, mild intoxication, and "heart palpitations". Most of the workers had been exposed for an average of two years, although the exposure was not to pure methylene chloride but rather to about 78 % methylene chloride with the remainder of the mixture made up of methanol, triphenylphosphate, and dibutylphthalate.

On more careful inquiry, 72 % of the workers complained of headache and 50 %, of increased fatigue. 49 % had irritation of the upper respiratory tract and conjunctiva, and 30 % had digestive disorders, (13).

### 13.3.4.2 HEMATOPOIETIC SYSTEM

No reports on significant effects on the hematopoietic system have been found.

#### 13.3.4.3 NERVOUS SYSTEM

In sixty male volunteers, age 20 to 30, cirtical flicker frequency (CFF) decreased to approximately the same end point under exposure at both 300 parts per million and 800 parts per million, but

at higher concentration, the decrease was much more rapid than at the lower concentration, Fodor et al, 1971 (27).

In a further series of experiments, 18 volunteers were exposed to concentrations of 317, 470 and 751 parts per million. The exposures lasted three to four hours and showed a response proportional to the exposure level, with a decrease in CFF, auditory vigilance, and decreased performance of psychomotor tasks when compared with controls, Winneke, 1974 (28).

In studies with eleven male subjects ranging in age from 23 to 43 years, exposure to methylene chloride in concentrations from 213 to 986 parts per million reported no unusual feelings at 514 parts per million for one hour. However, three subjects exposed to methylene chloride at 986 parts per million for two hours reported the odor to be moderately strong but they experienced no sensory irritation. Two of the subjects reported lightheadedness after one hour of exposure. There was rapid recovery after the exposure ceased (13).

#### 13.3.4.4 RENAL SYSTEM

No reports of adverse effects on the renal human system due to exposure to methylene chloride have been found.

#### 13.3.4.5 GASTROINTESTINAL TRACT

No reports of adverse effects on the gastrointestinal tract due to methylene chloride exposure have been found.

## 13.3.4.6 LIVER

In fatal cases of exposure to methylene chloride, slight enlargement of the liver has been reported. No evidence of liver dysfunction at lower levels of methylene chloride exposure has been found.

## 13.3.4.7 CARDIOVASCULAR SYSTEM

No reports of effects of methylene chloride on the carciovascular system have been found beyond those due to elevated carboxyhemoglobin levels.

#### 13.3.4.8 RESPIRATORY SYSTEM

As noted above, persons exposed to methylene chloride in the presence of open flames or very hot surfaces, may suffer from pulmonary edema due to decomposition of the methylene chloride to form phosgene.

In one case report of a 52 year old painter working in a small room where the windows were closed, and a kerosene stove in use, the man is reported to have worked for several hours, after experiencing a burning sensation in his throat. Later in the day, he was admitted to hospital with shortness of breath and cyanosis. Death occurred a few hours after admission. Autopsy revealed extensive degenerative changes in the epithelium of the trachea and the bronchi, together with hemorrhagic, edematous, focal pneumonia, Gerritsen et al, 1960 (29).

## 13.3.4.9 REPRODUCTIVE SYSTEM

No reports of the effect of methylene chloride on the human reproductive system have been found.

### 13.3.4.10 EYES AND OTHER SENSE ORGANS

The odor threshold for methylene chloride has been reported to be 214 parts per million, Leonardos et al, 1969 (30).

A number of occupational studies in workers exposed to methylene chloride have reported irritation of the eyes and respiratory tract, Moskowitz et al, 1952 (31), Hughes, 1954 (32).

### 13.3.4.11 CARCINOGENICITY

No reports suggesting carcinogenic activity of methylene chloride in humans has been found.

## 13.3.4.12 MUTAGENICITY

No reports of the mutagenicity of methylene chloride in humans has been found.

#### 13.3.4.13 TERATOGENICITY

No reports of the teratogenicity of methylene chloride in humans has been found.

### 13.3.4.14 FACTORS AFFECTING HUMAN RESPONSE

Apart from the expected findings that the work rate affects the absolute amount of methylene chloride absorbed, no other documented factors have been found affecting methylene chloride toxicity. Exposure of humans to both methylene chloride and carbon monoxide has been assumed to be additive but no reports of experiments or of case studies in which exposures to both carbon monoxide and methylene chloride have occurred, have been found.

# 13.4 CHLOROFORM

## 13.4.1 SUMMARY OF BIOLOGICAL INFORMATION

Irritant to eyes, nose and throat. Central nervous system depressant. Liver damage reported after 1-4 years exposure to 2-205 ppm range. Lassitude reported at 23-35 ppm for 4 hours per day. Fetal abnormalities in rats reported at 30 ppm. At one half maximum tolerated dose, chloroform causes liver cancer in rats. Occupational limit 10 ppm.

Carcinogen at high levels in rats. Liver damage in humans.

Toxicity Rating: [A]

Toxicity to Animals

Test Rating

Acute Moderate

Chronic High

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological High

## 13.4.2 METABOLISM

When carbon 14 labelled chloroform was given by intraduodenal lavage at a dose of 1 ml/kg of body weight it was found that 18 hours after dosing 74 % of the radioactivity from chloroform had appeared in the exhaled air as chloroform and 3.6 % as carbon dioxide. In further experiments no more than 5 % of the chloroform administered

was metabolized to carbon dioxide, Paul et al, 1963 (33).

In further experiments with C14 labelled chloroform the radioactive carbon appeared in the amino-acid fraction corresponding to
methionine whereas labelled carbon from methylene chloride and methyl
chloride was found in the amino-acid fraction corresponding to serine,
Reynolds et al, 1967 (4). Studies in rats that were fasted for 10
hours and then exposed to 10,000 parts per million of chloroform for
a period of 5 hours produced gross enlargement of the centrilobular
hepatic cells. The cells also showed pallor and upon appropriate
staining of frozen sections fatty degeneration was demonstrated.
Electron microscopy showed that chloroform produced early dilation of
the granular endoplasmic reticulum with detachment of the rivosomes
producing a marked reduction of centrilobular protein synthesis.
From these experiments it was concluded that the toxic effect of
chloroform on the liver can be explained by the formation of toxic
metabolites by hydroxylating enzyme systems, Scholler, 1968 (34).

It may therefore be concluded that at the molecular level the fatty infiltration of the liver that has been such a classical feature of chloroform intoxication is due to homolytic dissociation of the C-C1 bond, with the polyenoic fatty acids of the membranes of the smooth endoplasmic reticulum being attacked by the free radical products.

In support of this mechanism of liver damage by chloroform is the observation that cysteamine, which is considered to protect against homolytic damage caused by ionizing radiation, also protects against

liver necrosis, fatty infiltration and glucose-6-phosphatase inhibition brought about by carbon tetrachloride, Hathway, 1974 (35).

## 13.4.2.1 ABSORPTION

Chloroform is well absorbed by the skin, mucous membranes and lung, Lehmann et al, 1943 (8).

## 13.4.2.2 DISTRIBUTION AND RETENTION

Many investigations have been made on the distribution of chloroform.

It has been found that the saturation of the blood depends upon the partial pressure of the inhaled chloroform and the rate and depth of respiration.

## 13.4.2.3 ELIMINATION

Elimination of chloroform begins as soon as absorption ceases or the level of exposure decreases. About seven hours after anaesthesia with chloroform the blood is practically free of the compound the final portions being eliminated 24 hours after the end of the exposure. About 80 to 95 per cent of chloroform is eliminated through the lungs with a small percentage eliminated through the kidneys.

# 13.4.3 ANIMAL EXPERIMENTAL STUDIES

# 13.4.3.1 HEMATOPOIETIC SYSTEM

No reports of significant effects of chloroform upon the hematopoietic system were found.

### 13.4.3.2 NERVOUS SYSTEM

In mice exposed to a variety of concentrations of chloroform narcosis was produced in 10 minutes at a level of 7,400 parts per million, in half an hour at 6,800 parts per million, in three-quarters of an hour at 4,000 to 6,000 parts per million and in one hour at 4,000 parts per million. At levels of 2,500 to 2,700 parts per million there was some loss of reflexes and light narcosis among some of the animals.

In cats light narcosis was produced at a level of 7,200 parts per million after 78 minutes of exposure and deep narcosis after 93 minutes. Levels of 22,000 parts per million of chloroform produced light narcosis after 10 minutes and deep narcosis after 13 minutes (36).

## 13.4.3.3 RENAL SYSTEM

Chloroform in non-lethal doses may produce renal dysfunction in animals. Different strains of mice vary widely in their susceptibility to the nephortoxic action of chloroform.

Microscopic examination of kidney sections shows a correlation between the percentage of mice in each group showing abnormal kidney function tests and the percentage showing necrosis of the proximal tubules. The median effective dose of chloroform for significant PSP excretion was 0.12 ml/Kg of body weight and for increasing urinary protein and glucose, it was 0.07 ml/Kg of body weight, Plaa et al, 1965 (37).

## 13.4.3.4 GASTROINTESTINAL TRACT

Chloroform is readily absorbed from the gastrointestinal tract producing systemic toxicity but no reports of local effects on the gastrointestinal tract have been found.

## 13.4.3.5 LIVER

Chloroform, mole for mole is generally accepted to be less hepatotoxic than carbon tetrachloride which is the model halogenated hydrocarbon liver toxicant. Nothnagel was the first to observe injuries caused by chloroform, Lehmann et al,(8). The hepatotoxic effects of chloroform can occur after ingestion, inhalation or intravenous injection.

In mice the dose of chloroform that just produces minimal, mid zonal, fatty change in the liver has been found to be 35 mg/Kg body weight when the chloroform was administered by tube into the esophagus. In the same experiment in rats minimal, central fatty liver change was found at a dose of 70 mg/Kg of body weight and massive fatty infiltration at 140 mg/Kg, Jones et al, 1958 (38).

In mice exposed to chloroform by inhalation moderate fatty infiltration of the liver was found after four hours of exposure at 100
parts per million when the animals were killed one to three days after
the exposure. The liver changes were seen more frequently in mice
killed on the day after the exposure than in those sacrificed after three
days. The liver damage was proportional to the concentration of



chloroform over a range from 200 to 800 parts per million and was associated with microscopically demonstrable liver necrosis and an increase in activity of serum ornithinecarbamoyl transferase, Kylin et al, 1963 (39).

# 13.4.3.6 CARDIOVASCULAR SYSTEM

Chloroform is capable of sensitizing the heart to circulating catecholamines and thereby producing ventricular arrhythmias in animals and man. See Section 13.4.4.7.

## 13.4.3.7 RESPIRATORY SYSTEM

At lethal levels of chloroform exposure the lungs are engorged with blood and may show patchy necrosis and hemorrhage. At lower levels of chloroform exposure no reports of pulmonary damage have been found.

### 13.4.3.8 REPRODUCTIVE SYSTEM

Although studies of the teratogenicity of chloroform have been carried out no complete study of the effect of chloroform on reproduction has been found.

## 13.4.3.9 ENDOCRINE SYSTEM

No reports of the effect of chloroform on the endocrine system have been found.

### 13.4.3.10 EYES AND OTHER SENSE ORGANS

At high concentrations chloroform is an irritant to the eyes and

mucous membrane. Liquid chloroform instilled into the eyes of three rabbits caused slight irritation of the conjunctiva, which was barely detectable one week after treatment. In addition, slight but definite corneal injury occurred as demonstrated by staining with fluorescein. Purulent exudate occurred two or more days after treatment, Torkelson et al, 1976 (40).

## 13.4.3.11 CARCINOGENICITY

Highly significant increases in hepatocellular carcinoma were observed in both sexes of mice given chloroform five time a week for 78 weeks at a dose of 100 and 200 mg/Kg of body weight for males and 200 and 400 mg/Kg of body weight for female mice. These levels were increased after 18 weeks to 150 and 300 mg/Kg body weight for males and 250 and 500 mg/Kg of body weight for females. Nodular hyperplasia of the liver was observed in many low dose male mice that had not developed hepatocellurlar carcinoma. Rats were also exposed in the same manner to similar concentrations of chloroform and showed 24 % renal epithelial tumors in the high dose group, 8 % of such tumors in the low dose level and no such tumors in the control animals, Page, 1976 (41).

#### 13.4.3.12 MUTAGENICITY

Information on the mutagenicity of chloroform is scanty. Chloroform has given negative results when tested with microsomal incubates with S. typhimurium T.A. 1535 and E. coli K-12 for base pair substitution

and S. typhimurium T.A. 1538 for frame-shift mutations, Uehleke et al, 1976 (42).

#### 13.4.3.13 TERATOGENICITY

In studies of rats exposed to 30, 100, or 300 parts per million of chloroform for seven hours a day, five days a week on day six through fifteen of gestation showed a significant increase in fetal abnormalities at the 100 and 300 parts per million level although the 300 part per million results were confused by changes in dietary intake. At the 100 parts per million level there was a significant increase in the incidence of acaudia, imperforate anus, subcutaneous edema, missing ribs and delayed skull ossification. The rats exposed to 30 parts per million of chloroform only showed significant increases in the incidence of wavy ribs and delayed skull ossification.

When chloroform was given by mouth to rats and rabbits there was no evidence of teratogenicity in either species at any dosage level tested but in both species reduced birth weights were observed with the highest dosages administered. (126 and 50 mg/kg to the rats and rabbits respectively.)

#### 13.4.3.14 FACTORS AFFECTING TOXICITY

#### 13.4.3.14.1 TOLERANCE

In the experiments previously referred to in which hepatomas were induced in mice by repeated oral administration of chloroform,

Eschenbrenner, 1945 (43). Necrotic areas were observed in the kidneys

of the male mice but not of female mice receiving doses of 0.2 and 0.1 microlitres of chloroform/Kg of body weight. Other experiments have shown that removal of the testes protects male mice from renal necrosis due to chloroform and that the administration of testosterone to ovariectomized females rendered them susceptible to the effect of chloroform on the kidney. It therefore appeared that testosterone was essential for the development of the chloroform induced renal tubular necrosis and this was confirmed in later studies, Krus et al, 1975 (44). From these experiments it may be said that female mice are more tolerant of chloroform than male mice although the significance of this for human health remains to be demonstrated.

## 13.4.3.14.2 SUSCEPTIBILITY

As mentioned in the preceding section male mice are more susceptible to renal tubular necrosis due to chloroform than are female mice.

Pre-treatment with Phenobarbital potentiates the action of chloroform on the liver, Scholler, 1970 (45).

In the presence of high circulating levels of Epinephrine, chloroform, in common with a number of halogenated anaesthetic agents, produces ventricular arrhythmias in dogs, Kilmore et al, 1971 (46).

Alcohols, barbiturates and D.D.T. when given prior to chloroform exposure increase the toxic effects of chloroform on the liver. The effects of these compounds are consistent with the induction of hepatic microsomal enzyme activity, Kutob et al, 1961 (47), Sipes et al, 1973 (48), Dingell et al, 1968 (49), McLean, 1970 (50). That the susceptibility

of some animals to chloroform is genetically determined is shown by the fact that mice of the C57 BL/6J strain are about four times more resistant to the lethal effects of chloroform than the DBA/2J strain. Results of these and other tests suggest either single gene intermediate inheritance or multifactorial genetic control over chloroform toxicity.

Resistance to chloroform has been reported to behave as a dominant trait, all males of the C3H/He strain died from an injection of chloroform at 0.18 mg/Kg of body weight whereas those of the C57BL/6JN strain and the F1 hybrid between these strains survived. At high chloroform doses all mice developed hepatic toxicity whereas strain differences in LD50 values involved primarily the dose at which renal damage caused death. Sex hormones have been implicated in the sex difference in renal toxicity, immature male mice and castrated adult male mice are resistant to chloroform induced damage but are sensitized by testosterone. It has been suggested that mouse strain differences in androgen production and functioning may account for the strain differences in the reported LD50 studies, Hill et al, 1975 (51).

## 13.4.3.14.3 AGE

As mentioned in the previous section immature male mice are resistant to chloroform induced renal toxicity compared with mature male mice.

#### 13.4.3.14.4 SEASONAL VARIATIONS

No reports of seasonal variations in toxicity due to chloroform have been reported.

### 13.4.3.14.5 NUTRITION

No reports of the effect of nutrition on chloroform toxicity were found.

# 13.4.3.14.6 HEALTH OF THE INDIVIDUAL

Although it would be expected that pre-existing disease particularly of the liver and kidney would render animals more susceptible to chloroform toxicity, no reports of such effects have been found except those reported under 13.4.3.14.8.

## 13.4.3.14.7 INTERACTION WITH OTHER CHEMICALS

See Sections 13.4.3.14.1 and 13.4.3.14.2.

## 13.4.4 HUMAN EXPERIENCE

### 13.4.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

Because chloroform has been used for many years as an anaesthetic agent a great deal of empirical information has been acquired about the effects of this chemical in humans. Chloroform produces anaesthesia at a level of about 20,000 parts per million although the exposure during the induction period of anaesthesia is usually to concentrations of about 30,000 parts per million which is reduced as full anaesthesia develops.

In contrast to the many reports on use of chloroform as an anaesthetic agent there are relatively few reports of studies among industrial workers exposes to the compound.

In a study of workers in England manufacturing confectionery there were complaints of lassitude, flatulence, dyspepsia, dry mouth, thirst, depression and irritability. Attempts to reduce these complaints by reducing the exposure through reduction of working hours was not successful. Finally the operators refused to work on that particular process. Later a new team of operators were engaged and a system of exhaust ventilation was installed after which the work proceeded without further interruption. Attempts to reconstruct the concentrations of chloroform existing before the introduction of ventilation gave figures ranging from 155 to 161 parts per million during the simulated poor ventilation period to levels ranging from 23 parts per million to the single value of 1,163 parts per million measured under the conditions existing at the time of the report. From the environmental measurement it is difficult to come to any conclusion about the exposure of the employees to chloroform. In three groups of workers the first of whom were employed during the period of severe complaints, the second consisted of the employees brought in to replace the long service employees, and a third group who worked in other departments of the firm and who served as a control group showed no difference in liver function of clinical examination, (36).

In a report from Poland, 294 workers who used chloroform in a pharmaceutical factory were studies by means of a complete medical history, physical examination and liver function tests. The method of reporting of this study and the scanty levels of chloroform between the exposure to chloroform and the clinical state of the workers, (36).

## 13.4.4.2 HEMATOPOIETIC SYSTEM

No reports of effects of chloroform on the intact human hematopoietic system were found.

#### 13.4.4.3 NERVOUS SYSTEM

In addition to the extensive experience following the use of chloroform for surgical anaesthesia, some experiments have been reported in which humans have been exposed to graduated levels of chloroform. At levels of 7,200 parts per million during 15 minutes exposure to chloroform the intoxication was so marked that it was considered unsafe to continue to higher concentrations in the human volunteers, (8).

Cases of solvent abuse have been reported including one case of a 33 year old man who habitually inhaled chloroform over a period of 12 years. The psychiatric and neurologic symptoms reported in this were depression, loss of appetite, hallucinations, ataxia, and dysarthria. In a case report of a 19 year old male who mistakenly drank unknown quantity of chloroform after consuming three bottles of beer the ingestion of the chloroform was followed by collapse and on

being examined in the local hospital he was found to be stuporous and cyanotic. Liver function tests became grossly abnormal by the third day following admission but were beginning to return to normal by the sixth day, and were completely normal eight weeks after discharge. The patient remained unconscious for three days and then began to respond but showed some cerebellar damage characterized by instability of gait and slight tremor of finger to nose testing.

The cerebellar abnormalities returned to normal in two weeks, Storms, 1973 (52).

## 13.4.4.4 RENAL SYSTEM

Although the effect of chloroform on the liver have overshadowed the effects on other organs, apart from the brain, evidence of renal damage has been reported in a number of cases of chloroform intoxication. This damage has usually taken the form of albumin and red blood cells being found in the urine with elevated blood urea levels and necrosis and fatty degeneration of the kidney, (36).

#### 13.4.4.5 GASTROINTESTINAL TRACT

No reports of adverse effects of chloroform upon the gastrointestinal tract have been found.

#### 13.4.4.6 LIVER

The first two cases of jaundice and death following the administration of chloroform were reported by Heyfelder in 1848. This means that hepatic dysfunction and damage as a complication of anaesthesia and surgery date back to the beginning of the use of anaesthesia itself. Following the assembling of 30 isolated case reports of liver damage following anaesthesia and surgery during the early years of this century coupled with studies of the effects of chloroform in the dog the American Medical Association recommended in 1912 that "the use of chloroform as the anaesthetic for major operations is no longer justifiable".

Following many studies of anaesthetic drugs both in man and in animals it appears generally accepted that transient, subclinical abnormalities in the results of liver function tests commonly develop following surgery. The severity of the abnormalities appear to be related to the magnitude of the surgical procedure but not to the anaesthetic agent and it seems probable that the changes in liver function represent the combined effects of surgery and anaesthesia rather than a specific toxic effect of the anaesthetic agent employed, Dykes, 1973 (53).

Following the American Medical Association statement on the use of chloroform its use steadily declined although chloroform continues to be used by some anaesthetists until the present time. No satisfactory epidemiological study of the effects of chloroform on the liver have been carried out although when isolated case reports of hepatic damage following the administration of Halothane appeared, nine retrospective

cohort studies were undertaken to attempt to provide an adequate epidemiological evaluation of the problem. Following the results of these epidemiological tests the only compelling evidence for the existence of Halothane hepatitis remains two reports of demonstrated liver function changes as a result of exposure to minimal quantities of Halothane, Klatskin et al, 1969 (54), Johnston et al, 1971 (55).

Liver damage following obstetrical delivery using chloroform has been repeatedly reported, Gibberd, 1935 (56), Royston, 1924 (57). Typically such cases of liver damage were characterized by a latent period of a few hours to a day following delivery when drowsiness, restlessness, jaundice and vomiting would begin followed by fever, tachycardia, liver enlargement, abdominal tenderness, delirium, coma and abnormal liver and kidney function tests. In fatal cases the liver was bright yellow in color and on microscopic examination showed fatty infiltration with centrilobular necrosis.

In evaluating such case reports it must be remembered that it was usual to give chloroform as an analgesic during the second stage of labor and chloroform was often used as the anaesthetic agent during the actual delivery. Therefore obstetrical patients were exposed to chloroform over relatively long periods of time. Liver damage has also been reported following surgical procedures of relatively short duration (35 minutes) and after accidental ingestion of chloroform with jaundice, liver enlargement and vomiting.

## 13.4.4.7 CARDIOVASULAR SYSTEM

Arrhythmias due to chloroform have been reported since the earliest days of chloroform anaesthesia. Such arrhythmias have been found with exposure to other chlorinated hydrocarbons and in particular exposure to trichloroethylene. A number of other anaesthetic agents are also known to produce irregularities of cardiac rhythm.

Where the level of chloroform given during anaesthesia was carefully controlled, the irregularities of cardiac rhythm were less common, Whitaker et al, 1965 (58).

## 13.4.4.8 RESPIRATORY SYSTEM

No reports of an effect of chloroform upon the respiratory system has been found except in those cases where deep coma resulted in severe respiratory depression.

#### 13.4.4.9 REPRODUCTIVE SYSTEM

No reports of the effect of chloroform upon the human reproductive system have been found.

#### 13.4.4.10 ENDOCRINE SYSTEM

No reports of chloroform upon the human endocrine system have been found.

## 13.4.4.11 EYES AND OTHER SENSE ORGANS

Chloroform is mildly irritant to the eyes and upper respiratory tract. As with other chlorinated hydrocarbon solvents olfactory fatigue

rapidly sets in following exposure and the sense of smell therefore serves as a poor warning of dangerous levels of the chemical.

# 13.4.4.12 CARCINOGENICITY

No reports of cancer due to chioroform have been found.

# 13.4.4.13 MUTAGENICITY

No reports of mutagenicity in humans due to chloroform exposure have been found.

## 13.4.4.14 TERATOGENICITY

No reports of teratogenicity due to exposure to chloroform have been found.

## 13.4.4.15 FACTORS AFFECTING HUMAN RESPONSE

No reports of unusual sensitivity or tolerance to chloroform have been found.

## 13.5 CARBON TETRACHLORIDE

### 13.5.1 SUMMARY OF BIOLOGICAL INFORMATION

Central nervous system depressant. Liver damage in man at around 10 ppm. Restriction of visual fields in man at about 5 ppm. At levels causing severe liver damage, liver cancer found in rats, mice and hamsters. No clear evidence of mutagenicity. Occupational level 2 ppm (TWA). Odor threshold 20-100 ppm.

Carcinogen in rats; causes visual and liver damage in man at low levels.

Toxicity Rating: [A]

Toxicity to Animals

Test Rating

Acute Moderate

Chronic High

Toxicity to Man

Test Rating

Experimental

Epidemiological High

### 13.5.2 METABOLISM

There is considerable evidence that the toxicity of carbon tetrachloride is associated with its metabolism. The in vitro conversion of carbon tetrachloride to chloroform in the liver of the

rat has been reported and the production of carbon dioxide from C14 labelled carbon tetrachloride has also been demonstrated, Butler, 1961 (59), McCollister et al, 1951 (60), Rubinstein et al, 1964 (61).

The in vitro conversion of carbon tetrachloride to chloroform as the result of homolytic cleavage results in the production of free radicals and causes lipoperoxidation and necrosis of the liver, Fowler, 1969 (9), Ugazio et al, 1973 (11).

In support of this mechanism of liver damage by carbon tetrachloride is the observation that cysteamine, which is considered to protect against homolytic damage caused by ionizing radiation, also protects against liver necrosis, fatty infiltration and glucose-6-phosphatase inhibition brought about by carbon tetrachloride, Hathway, 1974 (35).

High doses of carbon tetrachloride will inhibit the hepatic metabolizing enzyme system, Dingell et al, 1968 (49), Sasame et al, 1968 (62).

The inhibition of this enzyme system greatly increases the resistance of rats to carbon tetrachloride poisoning thus even relatively low doses of carbon tetrachloride will increase the resistance of rats to subsequent additional doses of the compound, Glende, 1972 (63).

If rather than being inhibited the hepatic metabolizing enzyme system is induced, carbon tetrachloride toxicity is greatly increased, Cornish et al, 1973 (64).

The fact is that both carbon tetrachloride and chloroform show potentiation by phenobarbital but such potentiation has been shown not

to occur with methylene chloride, methyl chloroform, trichloroethylene and perchloroethylene. The known major metabolites of the solvents whose toxicity is not potentiated by phenobarbital are the readily excreted alcohols and acids. In contrast to these products is the prediction of the production of free radical intermediates in the case of carbon tetrachloride and chloroform metabolism. This marked difference in the metabolic pathway of halogenated solvents provides an explanation for the markedly different effect of inducers of microsomal enzyme That the stimulation of microsomal enzyme activity by carbon activity. tetrachloride might be of significance for human health is suggested by experiments in which carbon tetrachloride was inhaled at a concentration of 50 parts per million for 28 days. There was significant increase in the liver content of cytochrome P-450. Whether lower concentrations of carbon tetrachloride for longer periods of exposure would also cause enzyme induction, is not known, Norpoth et al, 1974 (65).

#### 13.5.2.1 ABSORPTION

Carbon tetrachloride is easily absorbed by the gastrointestinal tract and lung while the question of skin absorption appears more controversial. Lehmann and Flury in their book, 'Toxicology and Hygiene of Industrial Solvents' state that carbon tetrachloride is readily absorbed by the skin while studies of the absorption through skin of rabbits' ears suggested that fairly long exposure times might be required for significant absorption to occur, Lapidus 1929 (66),



McCord, 1932 (67).

Studies of the absorption of carbon tetrachloride through the skin of the thumb were carried out in three subjects, each of whom immersed on thumb in carbon tetrachloride for thirty minutes and the concentration of carbon tetrachloride in the exhaled air of the subjects was determined at 10, 20 and 30 minutes of immersion. The concentrations of carbon tetrachloride in the exhaled air showed a graded increase according to the duration of the immersion of the thumb. After thirty minutes of immersion the exhaled air concentration ranged from 0.69 to 5.23 µg. of carbon tetrachloride per litre of air. Carbon tetrachloride was still measureable in the exhaled air of the subjects five hours later, (36).

## 13.5.2.2 DISTRIBUTION AND RETENTION

There is little information in the literature on the distribution and retention of carbon tetrachloride but there is evidence that absorption, distribution and retention vary considerably between the various halogenated hydrocarbons, Astrand, 1975 (68).

#### 13.5.2.3 ELIMINATION

Most absorbed carbon tetrachloride is excreted through the lungs unchanged while a minor amount is metabolized. Although only a small amount is metabolized, it appears likely that it is this fraction that is chiefly responsible for the toxic effects of carbon tetrachloride.

# 13.5.3 ANIMAL EXPERIMENTAL STUDIES

## 13.5.3.1 HEMATOPOIETIC SYSTEM

No reports of significant effects of carbon tetrachloride exposure on the hematopoietic system were found.

### 13.5.3.2 NERVOUS SYSTEM

Carbon tetrachloride was introduced as an anesthetic agent in 1865 by Simpson but the compound fell into disuse about 10 years later apparently because of its serious effects upon the cardiovascular system rather than any hepatoxicity, Dykes, 1973 (53). Since that time there has been ample evidence that carbon tetrachloride is a powerful central nervous system depressant whether the compound is inhaled or swallowed. Because of the more serious toxic effects on the liver and the kidneys, relatively less attention has been paid to the effect of carbon tetrachloride on the nervous system.

#### 13.5.3.3 RENAL SYSTEM

Several aliphatic chlorinated hydrocarbons solvents and carbon tetrachloride in particular, have important toxic effects on the kidneys, Von Oettingen, 1964 (2). Although the mechanisms by which the aliphatic chlorinated hydrocarbons exert their nephortoxic effect is unclear, tolerance develops to the toxicity of these agents in a similar way to that shown in the liver. However, although both the kidney and the liver show the development of tolerance after exposure to carbon tetrachloride the mechanism by which this tolerance is developed may well be different in the two tissues since there is little evidence

that the nephrotoxic action of carbon tetrachloride results from metabolites rather than the parent compound. Because of the relatively short half-life of free radicals, it would be expected that they would have to be produced in the organ where their toxic effect is demonstrated. It is therefore relevant that rat kidney slices are much less active in metabolizing C-14 labelled carbon tetrachloride than are liver slices, Watrous et al, 1972 (69).

## 13.5.3.4 GASTROINTESTINAL TRACT

No reports of effects of carbon tetrachloride upon the gastrointestinal tract were found.

#### 13.5.3.5 LIVER

The characteristic effect of carbon tetrachloride upon the liver is to produce centrilobular liver necrosis. As discussed under 13.5.2 the action of carbon tetrachloride on the liver is thought to be mediated through the production of free radicals.

The qualitative and quantitative aspects of carbon tetrachloride damage in the liver and kidney have been studied in rats and it was found that marked changes appeared in the kidney some two hours before similar changes occurred in the liver. Severe renal damage was still seen 48 hours after the subcutaneous injection of carbon tetrachloride but 128 hours after injection the kidney had returned to a normal appearance. At this time severe damage was still present on microscopic examination of the liver. In animals given injections of low doses of

carbon tetrachloride every three days for 12 weeks, minimal changes were found in the kidney up to two weeks after the beginning of the injections whereas fairly severe changes were found in the liver.

After two weeks of injections, however, the repair processes could not be completed between injections and the kidney began to show permanent and severe renal damage whereas the liver cells had not shown recovery between any of the injections, Lundh, 1964 (70).

Three observations suggest that carbon tetrachloride itself is not responsible for the changes seen in the liver after absorption of carbon tetrachloride. These are the lack of coincidence between the structural and the functional changes, the lack of response of isolated organelles to direct addition of carbon tetrachloride and correlation of the liver damage with the level of drug metabolizing enzymes.

The structural changes that occur in animals exposed to carbon tetrachloride are rather uniform and independent of species. Similar although not indentical changes occur in man, monkeys, guinea pigs, and rats.

Within the first few hours after absorption of carbon tetrachloride, the liver shows swelling of the cells, fatty deposition, and dispersion of the ribosomes from the surface of the endoplasmic reticulum. In some of the cells towards the midzone a swelling and vesiculation of the endoplasmic reticulum occurs. The cells in the periportal zone show varying degrees of ribosomal dispersion. Increased levels of exposure to carbon tetrachloride increase the extent of the injury, and



cause cells more and more distant from the central vein to become affected.

The accumulation of fat in the liver cells is one of the classical features of carbon tetrachloride poisoning although not confined to that compound. Tracer techniques have shown that the source of the fat in the liver following chlorinated hydrocarbon poisoning is a decrease in lipid secretion from liver cells, not an increase in transport to liver cells. The fat is transported to the liver as fatty acid bound to albumin. In the liver the fat is absorbed from the plasma and esterified with glycerol to form neutral lipid. The excretion of neutral lipid requires a carrier protein and it has been shown that protein synthesis is reduced during carbon tetrachloride poisoning. Tracer studies have shown that the synthesis of at least two proteins is reduced as early as two hours following carbon tetrachloride administration. The exact mechanism by which the synthesis of protein is reduced is not known, Smuckler, 1976 (71).

Considering the vast amount of experimentation that has been conducted with carbon tetrachloride there have been surprisingly few studies upon which to base dose response and dose effect relationships. In an experiment in which 15 rats, 15 guinea pigs, 3 rabbits, 2 dogs, and 3 monkeys, were exposed to carbon tetrachloride at 82 parts per million for 8 hours a day, 5 days a week for a total of 30 exposures, weight losses or decreased growth occurred with all species under each exposure condition except for rats at 1 part per million. In a similar

experiment at a level 10 parts per million over a period of 90 days similar results were obtained (72). In chronic exposures of guinea pigs and rats to 5, 10, 25, 100, 200, and 400 parts per million of carbon tetrachloride for 7 hours a day, 5 days a week for 184 exposures over a period of 258 days, increased liver weights were found in guinea pigs at all levels of exposure with a moderate amount of fatty degeneration at 10 part per million and above and a moderate degree of liver cirrhosis at 25 parts per million and above. The rats showed increased liver weights at all exposure concentrations above 10 parts per million and liver cirrhosis was found at exposures above 50 parts per million, Adams et al, 1952 (73).

If, rather than looking at mortality data, the effect of carbon tetrachloride on the function of the liver is studied and compared with the results of other halogenated hydrocarbons, interesting comparisons can be made. If the following six halogenated hydrocarbons are ranked according to their relative potencies, then the 24 hour LD-50 is a poor index of the hepatotoxic potency of these compounds (1,1,2-tri-chloroethane, chloroform, trichloroethylene, tetrachloroethylene, carbon tetrachloride, 1,1,1-trichloroethane). Carbon tetrachloride appears to be one of the least potent halogenated hydrocarbons on the basis of the LD-50; however, if the level of BSP retention or SGPT elevation is used as the measurement, carbon tetrachloride becomes the most potent of the six halogenated hydrocarbons. The relative potencies for BSP and SGPT agree quite well with the known relative hepatotoxic potencies



of these halogenated hydrocarbon solvents based on industrial experience, Plaa, 1976 (74). If the potency ratio (LD-50/ED-50) are used for comparison purposes and SGPT elevation is used as the measurement of hepatic dysfunction, a potency ratio of 280 for carbon tetrachloride reflects the fact that the effective dose for producing liver injury in mice is about 1/300ths of the dose required to produce death. In contrast, the potency ratio for tetrachloroethylene is 1.0 indicating that the dose which produces liver injury is essentially identical to the dose that produces death. The practical significance of these observations is that if the concentration of a compound such as trichloroethylene is controlled to a level that will prevent evidence of central nervous system depression (dizziness, ataxia, etc.) this level of control will also prevent liver damage in the case of trichloroethylene since the potency ratio for this compound is about 1. However, with carbon tetrachloride control of the atmospheric concentration to prevent central nervous system effects does not eliminate the possibility that the concentration will cause liver injury, because of the large potency ratio for this compound, Plaa, 1976 (74).

# 13.5.3.6 CARDIOVASULAR SYSTEM

Although carbon tetrachloride when used as an anesthetic proved to be a potent cause of cardiac arrhythmias, Hardin, 1954 (75), few animal studies have been carried out on the cardiovascular effects of carbon tetrachloride.

#### 13.5.3.7 RESPIRATORY SYSTEM

Apart from secondary effects on the respiratory system which may result from high concentrations of carbon tetrachloride causing severe respiratory depression, no reports of specific effects of carbon tetrachloride on the respiratory system have been found.

#### 13.5.3.8 REPRODUCTIVE SYSTEM

In a two year feeding study using rats fed a diet containing carbon tetrachloride as a fumigant residue, the levels of carbon tetrachloride in the diet were 80 and 200 ppm. At this level no significant differences were found between the different groups either in growth or in feed consumption and feed efficiency. After six weeks on the experimental diets the three month old female rats were mated at about two monthly intervals. At parturition, litter size and weight were recorded and after ten days with the dams, the pups were again counted, the litters were weighed and the dams were returned to their communal cages. Although there was a very low parturition percentage in the fourth pregnancy, in the fifth pregnancy the high carbon tetrachloride group returned to normal and the number of parturitions was higher than that in the control group. The difference was therefore probably incidental. The size and weight of litters and the mortality rates of the pups was unaffected by the treatments.

In year two the fertility of the females dropped steadily and after five pregnancies only a few females from each group conceived.

The treatments had no effect on male fertility and in general seemed to have no effect on the reproductive activity of the rats of either sex. The conclusion of the authors was that at the level of carbon tetrachloride used no effects on growth, health or reproductive activity of the male or female rats was found, Alumot et al, 1976 (76).

## 13.5.3.9 ENDOCRINE SYSTEM

No reports of the effect of carbon tetrachloride upon the endocrine system have been found.

### 13.5.3.10 EYES AND OTHER SENSE ORGANS

Carbon tetrachloride is mildly irritating to the mucous membrane and upper respiratory tract when present in high concentrations.

## 13.5.3.11 CARCINOGENICITY

At levels that result in liver necrosis hepatomas have been reported in mice, rats and hamsters, IARC, 1972 (77).

There is no evidence that carbon tetrachloride causes tumors in any other organ than the liver or that tumors result from dosages of carbon tetrachloride below those resulting in liver necrosis.

120 daily doses of 6.25, 12.5, 25, or 50 microlitres per kilogram body weight of carbon tetrachloride when given to male and female mice resulted in hepatomas in all animals receiving the 12.5 microlitres per kilogram dose and above. These doses were known to cause necrosis of the liver whereas the 6.25 microlitres per kilogram dose was known not to cause liver necrosis, Eschenbrenner et al, 1946 (78).

Transplantation of tumors induced by carbon tetrachloride has succeeded in some cases, Edwards et al, 1942-43 (79).

Development of liver cell carcinomas in male and female Syrian golden hamsters after 30 weekly doses of a 5 % solution of carbon tetrachloride in corn oil administered by stomach tube, has been reported. The doses have been calculated to represent 0.125 and 0.625 millilitres per kilogram, (72).

#### 13.5.3.12 MUTAGENICITY

As with chloroform, information as to the mutagenicity of carbon tetrachloride is scanty. Carbon tetrachloride has been reported to give negative results when tested in E.coli and Salmonella typhimurium. A synergistic effect of carbon tetrachloride on the mutagenic effectiveness of cyclophosphamide in the host-mediated assay with S. typhimurium has been reported. Carbon tetrachloride did not affect the mutagenicity of cyclophosphamide when tested in vitro with S. typhimurium strains G46 and TA1950. Carbon tetrachloride was non-mutagenic when assayed in a spot-test with the above strains of S. typhimurium, Fishbein, 1976 (80).

#### 13.5.3.13 TERATOGENICITY

A significant decrease in fetal body weights and crown-rump lengths has been reported in rats exposed at 300 part per million of carbon tetrachloride on days 6 through 15 of gestation. Fetuses born to these rats showed no anatomical abnormalities by gross examination but the incidence of microscopic sternebral anamalies was significantly



increased by exposure at 1,000 parts per million. The conception rate, numbers of implantations, and litter sizes were normal, even though maternal body weights were significantly less than control body weights. This study was one of a number in which a variety of solvents were used and the results suggest that there was no correlation between the toxicity incurred by the mother and that by the embryo or fetus with the solvents used. The solvent which caused the least maternal toxicity, methylethyl ketone, showed a potential for producing terata. The compound which caused the greatest degree of maternal toxicity, carbon tetrachloride, did not produce terata. Chloroform caused both maternal toxicity and was highly toxic to the embryo and fetus, Schwetz et al, 1974 (81).

# 13.5.4 HUMAN EXPERIENCE

It is of interest that the earliest experience of adverse health effects from carbon tetrachloride resulted from the use of this compound as an inhalation anaesthetic. As early as 1867 unfavorable reports of the use of carbon tetrachloride as an anaesthetic agent appeared in the medical press, Smith, 1867 (82), Nunneley, 1867 (83).

Carbon tetrachloride was also used as a shampoo in beauty salons and in the home. At least one case of sudden death after the use of the compound in such a manner, may represent on of the earliest recorded cases of cardiac sensitization to circulating epinephrine with consequent ventricular arrhythmia, Veley, 1909 (84).

It was not until the early years of the 20th century that carbon

tetrachloride was used in the treatment of intestinal parasites. Its use as an oral medication for this purpose stimulated considerable research into the pharmacological effects of carbon tetrachloride in humans, Wells, 1924 (85). In a study in Ceylon carried out on condemned prisoners in 1922 and 1923 the prisoners were given varying doses of carbon tetrachloride 3 to 15 days before execution. Examination of the livers of the men at autopsy showed marked fatty degeneration in some and no detectable changes in others. No dose-response relationship could be determined but it is of interest that no fatalities occurred among the subjects within the 96 hours following ingestion of doses ranging from 3 to 8 millilitres of carbon tetrachloride (72).

# 13.5.4.1 EDIDEMIOLOGICAL AND CLINICAL STUDIES

Because the principal impact of carbon tetrachloride is upon the liver and kidney the clinical case studies will be reported under the appropriate organ system effects.

The number of epidemiological studies with even moderately adequate information about the levels of exposure to carbon tetrachloride are very few. In a study of 73 workers employed in fire extinguisher and carbon tetrachloride manufacture, 10 persons employed in dry-cleaning plants and 2 workers concerned with other uses of carbon tetrachloride, time-weighted carbon tetrachloride exposures ranged from 5 to 117 parts per million with peak exposures ranging from 22 to 1680 parts per million. On examination 9 of the men had definitely restricted visual fields and 26 men had slightly restricted

visual fields, while a further 40 had normal visual fields and no measurements were made on the 2 remaining men. Hematological studies, kidney function studies, and measures of liver function did not show significant abhormalities. 13 of the men showed an elevated icteric index, Smyth et al, 1975 (86).

In a group of 62 people working as locksmiths and carrying out cleaning operations with carbon tetrachloride, air analyses showed concentrations ranging from 6.4 to 9.5 parts per million. Among the 62 workers, 43 had reduced corneal sensitivity, 4 had restricted outer limits of visual field for white, 4 had subnormal or questionable dark adaptation curves, 15 had abnormalities of the color limits of their visual fields and in 7 there were changes in color perception, (72).

In a factory in which quartz crystals and other equipment were cleaned with carbon tetrachloride in a room divided by partitions, levels of carbon tetrachloride ranging from 67 to 97 parts per million were found on the side of the partition closest to the containers of carbon tetrachloride while on the other side of the partition levels ranging from 45 to 47 parts per million were measured.

17 of the 18 employees in the factory were interviewed and examined and 15 of the 17 interviewed had experienced one or more of the following: nausea, 15; anorexia, 12; vomiting, 7; flatulence, 7; gastric discomfort or distention, 10; and symptoms of headache or giddiness, 10. Nausea had usually developed on Tuesday or Wednesday of each week and vomiting on Thursday or Friday. Physical examination and

laboratory studies of the 17 employees revealed no abnormality and after corrective action was taken all workers were symptom free within one week and there was no recurrence after six months, Kazantzis et al, 1960 (87).

In a comparison of two groups of workers, one exposed to carbon tetrachloride used in the manufacture of polyfluorohydrocarbons and the other employed at the same plant but not exposed to carbon tetrachloride, serum bilirubin averaged 1.36 mg % in the exposed group compared with 0.46 mg % in the control group. The SGOT averaged 37.3 Sigma Frankel units in the exposed group and 32.7 Sigma Frankel units in the control group. Both the average zinc turbidity and average thymol turbidity of the exposed group were elevated compared to those of the control group. Urinary urobilinogen was found in 6 of those handling carbon tetrachloride and there was protein in the urine of 3 others in this group.

## 13.5.4.2 HEMATOPOIETIC SYSTEM

No reports of abnormalities of the hematopoietic system as a result of exposure to carbon tetrachloride have been found.

#### 13.5.4.3 NERVOUS SYSTEM

In a study of 6 workers using a mixture of 85 % carbon tetrachloride and 15 % methyl alcohol in a film coating operation all of the workers complained of fatigue after a few hours work even though the work was not physically demanding. The sense of fatigue continued during the working week but disappeared on weekends. Six samples of the work room

air averaged 79 parts per million carbon tetrachloride. It was considered that the complaints of fatigue were related to mild narcosis produced by the carbon tetrachloride exposure, Heimann et al, 1941 (88).

In an experimental study using two persons in a 10 cubic metre room in which concentrations ranging from 140 parts per million to 14,000 parts per million were generated, exposures ranged from 50 seconds to 30 minutes. At 240 parts per million for 20 minutes perception of a transient odor was the only effect reported. After 10 minutes exposure of 600 parts per million of carbon tetrachloride, dizziness and vertigo were experienced while exposures at 600 parts per million and above resulted in increasingly severe effects including headache, tiredness, giddiness and salivation. An exposure of 50 seconds at 14,000 parts per million resulted in loss of consciousness (72).

In 6 persons exposed to carbon tetrachloride at an average concentration of 49 parts per million for 70 minutes the detection of a slight but not unpleasant odor was the only nervous system response reported, Stewart et al, 1961 (89). In experimental exposure to 75 parts per million of carbon tetrachloride no adverse effects were reported after 5 hours of exposure while after 30 minutes of exposure at 320 parts per million, Davis, 1934 (90).

That exposure to carbon tetrachloride can cause transient interference with the function of the peripheral nervous system is suggested by the development of numbness of the ankles, knee, and thigh following exposure to a fine spray of liquid carbon tetrachloride during the process of cleaning bomb sights. The person involved also developed some weakness of the wrist and this symptom as well as the numbness showed rapid recovery following the cessation of the exposure, Farrell et al, 1944 (91).

### 13.5.4.4 RENAL SYSTEM

The nephrotoxicity of carbon tetrachloride has been attributed to its direct toxic effect on the proximal tubules or on the loop of Henle. Anuria occurs one to seven days after acute exposure by inhalation and is preceded by proteinuria. Anuria may last up to 15 days and dialysis has proved useful in treatment. Renal changes are confined to the tubules; the glomeruli are intact. The lesions may progress to hemorrhagic cortical necrosis. The proximal and distal convoluted tubules as well as the collecting tubules lining cells, Ehrenreicn, 1977 (92).

## 13.5.4.5 GASTROINTESTINAL TRACT

No reports of effects of carbon tetrachloride on the gastrointestinal tract have been found.

#### 13.4.5.6 LIVER

Death from carbon tetrachloride poisoning has most often been the result of the effect of the solvent on the liver. In many cases the fatal outcome appears to have been influenced by moderate to heavy



alcohol consumption.

In a typical case of carbon tetrachloride poisoning a laborer who had used the solvent for three hours to clean a machine in a large and well ventilated room developed nausea, giddiness, stomach pain, fever, and was hospitalized three days after exposure. Upon examination his liver was slightly enlarged and sensitive to pressure. Laboratory examinations showed an elevated SGOT level of 6,000 units per millilitre and serum aldolase of 300 units. The enzymes had returned to normal values 10 to 15 days after poisoning. A liver biopsy taken on the eighth day after intoxication showed large areas of centrilobular necrosis with the surrounding liver cells appearing normal.

Two men who used carbon tetrachloride in the cleaning of telephone relay equipment reported frequently experiencing nausea and stomach distress. Measurements of carbon tetrachloride concentrations made on 16 occasions showed values ranging from 10 to 100 parts per million. The older man had worked four years using carbon tetrachloride on an average of three days of week. During the forth year he developed pain in his right upper abdomen which forced him to cease work. Laparoscopy showed both lobes of the liver to be enlarged and yellow-red in color with indistinct markings. On microscopic examination of a liver biopsy fatty degeneration and moderate infiltration of the periportal areas was found. The SGOT was elevated and the BSP retention time was increased. No abnormal findings relating to kidney function were found (72). In experimental studies it was found that exposure to carbon tetrachloride

at about 10 parts per million for a duration of 180 minutes did not affect liver or kidney function as shown by normal urinary urobilinogen, SGOT, and 15 minutes phenolsulfonphthalein retention time. Exposure at 49 parts per million for 70 minutes, however, may have had a slight effect on liver function as shown by a reduction of serum iron one or two days later in two of four subjects in whom it was measured, Stewart, 1961 (89).

For a discussion of the relationship of carbon tetrachloride exposure to neoplasms of the liver see section 13.5.4.12.

### 13.5.4.7 CARDIOVASCULAR SYSTEM

Carbon tetrachloride, in common with other halogenated hydrocarbons, can cause serious and even fatal cardiac arrhythmias. The mechanism of action is not completely understood but it involves the sensitization of the myocardium to circulating epinephrine.

## 13.5.4.8 RESPIRATORY SYSTEM

No reports of direct effects of carbon tetrachloride on the respiratory system have been found although profound depression of respiration due to the central nervous system effects of carbon tetrachloride can lead to secondary changes in the lung.

#### 13.5.4.9 REPRODUCTIVE SYSTEM

No reports of the effect of carbon tetrachloride on human reproduction have been found.

### 13.5.4.10 ENDOCRINE SYSTEM

No reports of the effects of carbon tetrachloride on the endocrine system have been found.

## 13.5.4.11 EYES AND OTHER SENSE ORGANS

Peripheral constriction of the visual fields associated with carbon tetrachloride exposure have been reported in several studies. In some of these studies the effect has been most pronounced in the color field, Gray, 1947 (93), Wirtschafter, 1933 (94), Smith, 1950 (95). With regard to odor thresholds samples of carbon tetrachloride representing different modes of manufacture show variations in odor threshold concentration. Carbon tetrachloride manufactured by the chlorination of carbon disulfide has a lower threshold (21.4 parts per million) than carbon tetrachloride produced by the chlorination of methane (100 parts per million), Leonardos et al, 1969 (30).

High concentrations of carbon tetrachloride are irritating to the mucous membranes and upper respiratory tract.

#### 13.5.4.12 CARCINOGENICITY

Three human cases of hepatic carcinoma, two after repeated exposure, and one after a single exposure, have been reported. In each case, the diagnosis was confirmed at autopsy.

In one case a woman working as an assistant to a metallurgist cleaned metal several times a day with carbon tetrachloride. Two months after beginning work she became increasingly fatigued and showed

periodic jaundice. Thirteen months after the beginning of employment she was hospitalized at which time a large liver with nodular cirrhosis was found at operation. The woman then returned to work for a period of four months at which time she had to stop because of increasing weakness and jaundice. She died three years after beginning her work with the metallurgist. Cancer of the liver was confirmed at autopsy, Johnstone, 1948 (96).

A man who suffered severe acute carbon tetrachloride poisoning after sleeping in a room in which the rug had been cleaned with carbon tetrachloride, recovered after a hospital stay of nine weeks. When seen again four years later he had been in good health and clinical tests at this time were normal apart from a smooth, enlarged, non-tender liver. Three years after this examination he was readmitted to hospital complaining of anorexia, weight loss, nausea, vomiting and diarrhea. A tender mass was felt in the abdomen and an hepatocellular carcinoma was found by liver biopsy. The patient died five months later, Tracey et al, 1968 (97).

A fireman who was exposed to carbon tetrachloride used in fire extinguishers became intoxicated after destroying a swarm of wasps with a carbon tetrachloride extinguisher. After a period of 10 days of somnolence, anorexia and hematuria which were attributed to the acute effects of carbon tetrachloride he returned to work but suffered repeated episodes of fatigue, fever, hematuria and jaundice. Four years after the initial poisoning he was admitted to hospital when a liver



biopsy showed an early epithelioma of the liver. Two months after the biopsy the patient died and hepatic cancer was confirmed at autopsy, (72).

#### 13.5.4.13 MUTAGENICITY

No reports of the mutagenicity of carbon tetrachloride in humans have been found.

### 13.5.4.14 TERATOGENICITY

No reports of the teratogenicity of carbon tetrachloride in humans has been found.

### 13.5.4.15 FACTORS AFFECTING HUMAN RESPONSE

### 13.5.4.15.1 TOLERANCE

No reports of tolerance for carbon tetrachloride exposure in humans have been found.

#### 13.5.4.15.2 SUSCEPTIBILITY

Alcohol consumption has been considered by a number of investigators to play an important role in carbon tetrachloride poisoning. Alcohol was considered to be a predisposing factor in eight of ten cases reported in 1948, Abbott et al, 1948 (98). In another series, eight out of twelve cases were thought to involve alcohol as a predisposing factor, Joron et al, 1957 (99). In a series of 19 cases, 17 of them were considered to have alcohol as a contributing factor to the toxicity of carbon tetrachloride, New et al, 1962 (100).

## 13.5.4.15.3 AGE

No reports dealing with the effect of age in carbon tetrachloride poisoning have been found.

## 13.5.4.15.4 SEX

No reports suggesting a particular susceptibility to carbon tetrachloride poisoning in either sex have been found.

## 13.5.4.15.5 SEASONAL EFFECTS

No reports of seasonal effects in carbon tetrachloride poisoning have been found.

## 13.5.4.15.6 NUTRITION

No reports of the effect of nutrition on carbon tetrachioriae toxicity in humans have been found.

#### 13.5.4.15.7 HEALTH OF THE INDIVIDUAL

No specific reports of the interaction of pre-existing disease and exposure to carbon tetrachloride have been found in humans.

### 13.5.4.15.8 INTERACTION WITH OTHER CHEMICALS

Apart from the interaction of alcohol with exposure to carbon tetrachloride referred to above, no other specific reports of interactions between carbon tetrachloride and other chemicals have been found, although from animal studies it might be expected that concomitant exposure to phenobarbital and such other inducers of microsomal enzymes as DDT might tend to increase the toxicity of carbon tetrachloride.

### 13.6 DICHLORETHANE

Due to the paucity of toxicity information on 1,1-dichloroethane and 1,2-dichloroethane the format used in the majority of the documents on the health effects of selected chlorinated hydrocarbons will not be used and a general summary of the available information substituted.

### 13.6.1 SUMMARY OF BIOLOGICAL INFORMATION

Central nervous system depressant with wide spread harmful effects on clotting of blood. Liver damage and renal effects. Ethylene dichloride is a mutagen in bacterial tests. Occupational exposure level currently set at 5 ppm (TWA).

Mechanism of toxicity not well understood, but wide variety of organs and organ systems involved at low exposure levels. Not a proven carcinogen but under suspicion.

Toxicity Rating: [A]

Toxicity to Animals

Test Rating

Acute High

Chronic High

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological High



#### 13.6.2 EFFECTS IN ANIMALS

The LC-50 level for rats exposed to ethylene dichloride (EDC) has been reported as 48,600 mg/cu meter of air for 32 minute exposure and 4,048 mg/cu meter for a 432 minute exposure. The effects of inhalation exposures are similar in all mammals and are characterized by narcosis, pulmonary edema and mecrotic and hemorrhagic lesions of the liver and kidneys. Chronic exposure of rats, guinea pigs, rabbits and cats produced no apparent affects at a level of 400 mg/cu meter of air when the animals were exposed for 17 weeks, 6 hours a day, 5 days a week, Hoffman et al, 1971 (101). The maximum inhalation concentration tolerated for animals exposed for 7 hours a day, 5 days a week for six months was 1,600 mg/cu meter for rabbits, 800 mg/cu meter for rats, and 400 mg/cu meter for guinea pigs and rhesus monkeys, Johns, 1976 (102).

Exposure of dogs to 1,000 parts per million EDC for 7 hours produced a clouding of the cornea which was completely reversible on the cessation of exposure, Irish, 1962 (103). This clouding of the cornea is said to be characteristic of EDC and occurs not only in cases of inhalation but also after subcutaneous injection. The effect is thought to be connected with hydrolysis of EDC to glycol and hydrochloric acid and further oxidation to oxalic acid, (8). The clouding of the cornea has not been reported in man.

Subcutaneous injection of EDC at a dosage of 1 cc/Kg of body weight into rats produced an average mortality rate of 35 % in 24 hours, Highman et a), 1951 (104).

Rats, guinea pigs, rabbits and monkeys exposed to 100 parts per million of EDC for 168 days suffered no ill-effects.

The toxicity of EDC in mice is thought to be due to its metabolic breakdown which results in the formation of chloroacetate, Yllner, 1971 (105).

## 13.6.3 EFFECTS OF EDC IN MAN

The odor of EDC is just detectable at 50 parts per million but is not unpleasant in a 100-200 parts per million range, Browning, 1965 (106). Inhalation of high concentrations of EDC cause stupor, mental confusion, dizziness, nausea, vomiting and central nervous system depression. The symptoms are reversible upon cessation of the exposure. Few fatal cases of EDC poisoning have been reported. In one case a workman exposed to EDC while repairing a vessel used to transport the chemical became unconscious after an exposure lasting a few minutes. After being removed from the exposure he appeared to recover but several hours later became unresponsive and died. At autopsy there was considerable pulmonary edema, liver necrosis and meningeal hemorrage, Browning, 1965 (106). Ingestion of about 1-2 oz. of EDC has proved fatal in male adults, Lochhead et al, 1951 (107).

There have been few reported cases of chronic exposure of humans to EDC. In two cases reported in a plant using EDC as a solvent, one worker employed for nine weeks complained of weight loss, drowsiness and nervousness. The other subject employed for five months complained of upper abdominal pain and tremor of the tongue. Both complained of

nausea and vomiting. After removal from the exposure all symptoms disappeared, McNally et al, 1941 (108).

Ethylene dichloride is absorbed through the skin of mammals, but large doses are required to cause systemic poisoning. Ethylene dichloride was found to have no carcinogenic activity in inhalation exposures of rats, rabbits, guinea pigs and monkeys exposed to vapor concentrations of 405 620 mg/cu meter of air for periods ranging from 202 to 246 days. The study due to its relatively short duration cannot be considered definitive (109).

Ethylene dichloride is weakly mutagenic in salmonella typhi-murium TA1530 and TA1535 strains. Ethylene dichloride is non-mutagenic for TA1538 strain.

Ethylene dichloride (without activation) has also been recently shown to be an extremely weak mutagen in reverting the new tester strain TA100 which incorporates a resistance transfer factor (R factor).

Attempts to activate ethylene dichloride to a more mutagenic form using the standard rat liver S-9 mix for activation have been unsuccessful.

Ethylene dichloride has also been reported to be mutagenic in Drosophila. For an 8 hour treatment of the female Drosophila increased the frequency of recessive lethals, while 8 hour treatment with ethylene dichloride induced chromosome disjunction. Treatment of the nutrient medium with ethylene dichloride with prolonged contact of up to one day resulted in 25-30 % mutations with the effect more

pronounced in males than in females. Contact of only one hour resulted in mutation rates in Drosophila of about 2.6 %, Fishbein, 1976 (110).

# 13.6.3.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

A 14 year old boy who drank a few milliliters of 1,2-dichloroethane in the expectations of getting "high" showed deceptively few symptoms and signs on admission to hospital but his condition ran rapidly downhill and he died after five days. Prominent clinical features of this case were hypoglycemia and hypercalcemia. The late appearance and non-specificity of the clinical symptoms and signs have been noted in other cases of 1,2-dichloroethane poisoning, Hueper et al, 1935 (111), Yodaiken et al, 1973 (112), Hubbs et al, 1959 (113). Hypoglycemia may intervene at an early stage of intoxication and in the case of the teen-ager the hypoglycemia was mainly due to massive liver necrosis.

Blood coagulation became difficient largely because of depletion of liver-dependent factors. Despite the most sophisticated therapeutic measures the clotting problem was not reversed and the mechanism was not explained. Unexplained fibrinolysis has also been observed in trichloroethylene intoxication in the absence of significant liver damage, Musclow et al, 1971 (114).

#### 13.6.3.2 CARCINOGENICITY

The U.S. Environmental Protection Agency was officially notified by the National Cancer Institute in November, 1977 of the preliminary results of a 90 day rat and mouse feeding study. These preliminary findings showed squamous cell cancer of the fore-stomach and



hamangiosarcomas at many sites, for example, the liver and spleen.

Female rats showed mammary adenocarcinomata.

In the mouse the males showed hepatocellular carcinomata with lung adenomata. While the females showed mammary adenocarcinomata, lung adenomata and endometrial polyps.

In a further study at the United States National Cancer Institute ethylene chloride was given by gastric intubation to mice and rats of both sexes five times a week over a period of 78 weeks. The low dose in the rats was 50 mg/kg of body weight and the high dose of 100 mg/kg of body weight while in the mice the males received a low dose of 100 mg/kg of body weight and a high dose of 200 mg/kg of body weight, the female mice had a low dose of 150 mg/kg of body weight and a high dose of 300 mg/kg of body weight.

At the time of writing, this study was not complete but preliminary results indicated that ethylene dichloride was carcinogenic in both species. The male rats developed statistically significant numbers of squamous cell carcinomas of the fore-stomach as well as statistically significant number of hemangiosarcomas of the circulatory system. Female mice and rats on the other hand developed statistically significant numbers of mammary gland adenocarcinomas. The tentative conclusion of the report from the National Cancer Institute was that ethylene dichloride is a carcinogen in male and female rats and female mice.

## 13.6.4 1,1-DICHLOROETHANE

There was little published toxicity information on 1,1-dichloroethane and what information is published tends to be confusing with regard to the relative toxicity of the isomers.

In a study using rats, guinea pigs, rabbits and cats all the animals tolerated the inhalation of 500 parts per million of 1,1-dichloro-ethane without adverse effects over a period of 13 weeks. Rats, guinea pigs and rabbits tolerated an increase in the level of exposure to 1,000 parts per million for an additional 13 weeks but this level in cats resulted in kidney damage.

In similar experiments using 1,2-dichloroethane the highest level tolerated without evidence of toxicity was 100 parts per million for a 17 week period. Thus judging from the most sensitive animals 1,2-dichloroethane is about five times as toxic as 1,1-dichloroethane, Hofmann et al, 1971 (115). No other reports of human exposure or animal toxicity relating to 1,1-dichloroethane has been found.

## 13.7 1,1,1-TRICHLOROETHANE

## 13.7.1 SUMMARY OF BIOLOGICAL INFORMATION

Eye and nose irritant. Central nervous system depressant.

Respiratory tract irritant, because of irritation, occupational exposure limit is a "ceiling" limit of 350 ppm. Little evidence of chronic damage to humans or animals at levels below 1000 ppm. Central nervous system depression with giddiness and unsteadyness, prominent between 500-1000 ppm. Irritation of respiratory tract effectively determines exposure limit. Effects reversible below 1000 ppm.

Toxicity rating:

[C]

Toxicity to Animals

Test

Rating

Acute

Low

Chronic

Moderate

Toxicity to Man

Test

Rating

Experimental

Moderate

Epidemiological

Moderate

### 13.7.2 METABOLISM

Of the two trichloroethanes only the 1,1,1-isomer has been studied extensively with regard to its metabolic reactions. In two rats exposed to carbon 14 labelled 1,1,1-trichloroethane an average of 97.6 % of the administered dose was excreted unchanged in the exhaled air in

the 24 hours following the end of exposure. In three rats exposed to the labelled trichloroethane an average of 0.85 % of the administered radio-activity was found in the urine.

0.5% of the administered dose of radio-labelled compound was found as carbon dioxide in the exhaled air. Therefore in animals trichloroethane is not appreciable metabolized after inhalation, the majority of the compound absorbed being excreted unchanged through the lungs, Hake et al, 1960 (116). In rats inhalation of trichloroethane is followed by the excretion of small amounts of trichloroacetic acid and trichloroethanol, Ikeda et al, 1972 (117).

Dechlorination of 1,1,1-trichloroethane by the rat liver in vitro was found to be minimal, Van Dyke et al, 1971 (118).

When rats were exposed to 500 parts per million of trichloroethane for five days, seven hours a day there was no effect on the dechlorinating system and this reaction was not enhanced by exposure to methoxyflurane a microsomal enzyme inducer.

#### 13.7.2.1 ABSORPTION

Trichloroethane is rapidly absorbed from the lungs and in experiments in man using chlorine 38 labelled trichloroethane approximately 56 % of a 5 mg inhaled dose was retained one hour after inhalation of the trichloroethane in a single breath. The breath was held for 20 seconds to ensure maximum absorption, Morgan et al, 1970 (119).

Absorption of liquid 1,1,1-trichloroethane through the skin was studied by measuring the concentration of the compound in the exhaled air when one thumb had been immersed in the liquid for 30 minutes. The

maximum concentration of trichloroethane found in the expired air was 1.02 parts per million after 30 minutes of immersion, Stewart et al, 1961 (120).

Trichloroethane can be absorbed from the gut in humans although little quantitative information is available. In a person who drank loz. of l,l,l-trichloroethane the onset of nausea began about 30 minutes after the ingestion and apart from vomiting and diarrhea there were no abnormal clinical findings.

### 13.7.2.2 DISTRIBUTION AND RETENTION

Trichloroethane is chemically relatively stable and poorly soluble in blood. Of the seven solvents studied by Astrand, 1975 (68), 1,1,1-trichloroethane was the least soluble in blood having a blood/gas partition coefficient of 1.4 compared with a blood/gas partition coefficient of 32 for styrene. The solubility in blood obviously plays an important role in the transport of the solvent from the lungs to the tissues. Another important factor in the transport of the solvent is the metabolic rate which determines both the ventilation of the lung and therefore the delivery of the solvent to the alveolo-capillary membrane as well as the mass flow of blood available to carry the solvent from the lungs to the tissues. Because of the low solubility of 1,1,1-trichloroethane in blood this acts as a limiting factor in the transport and distribution of the solvent. The alveolar concentration of solvents is proportional to the solubility in the blood, being highest for the solvents with the least blood solubility. For this reason



1,1,1-trichloroethane had the highest alveolar concentration of the solvents studied by Astrand, 1975 (68).

Relatively insoluble substances such as 1,1,1-trichloroethane also reach equilibrium with arterial blood more rapidly than more soluble substances.

In a similar fashion the delivery of 1,1,1-trichloroethane to the tissues is dependent upon the transport of the solvent in the blood and the fat and water content of the tissue. 1,1,1-trichloroethane is relatively less soluble in the fat than such solvents as trichloroethylene, chloroform and toluene.

### 13.7.2.3 ELIMINATION

The principles governing the elimination of 1,1,1-trichloroethane are similar to those governing the uptake and distribution of the solvent. This has the important implication that because of the relatively poor transport of the solvent in the blood such transportation is a limiting factor in the compounds elimination. Thus, 1,1,1-trichloroethane was found at a level of 0.1 part per million in the breath of an individual one month after exposure to the mixture of 370 parts per million 1,1,1-trichloroethane 7 hours a day for 5 days,

Stewart et al. 1969 (121). 1,1,1-trichloroethane was also found in the alveolar air one month after exposure to 420 to 612 parts per million of 1,1,1-trichloroethane which had been inhaled for 6 1/2 to 7 hours a day for 5 days, Stewart et al, 1963 (122), Rowe et al, 1963 (123).

The very long time taken for excretion of 1,1.1-trichloroethane implies that on repeated exposure on consecutive days, as will occur in an occupational situation, not all of the solvent will be excreted by the beginning of the next work shift and therefore the body burden of 1,1,1-trichloroethane can be expected to build up during the working week. This is confirmed in the experiments of Stewart et al, 1963 (122).

### 13.7.3 ANIMAL EXPERIMENTAL STUDIES

### 13.7.3.1 HEMATOPOIETIC SYSTEM

No reports of adverse effects of trichloroethane on the hematopoietic system were found.

## 13.7.3.2 NERVOUS SYSTEM

l,l,l-trichloroethane has been used as an inhalation anaesthetic in man and animals and as such the period of induction is short and recovery from anaesthesia lasting 20-30 minutes occurred within 2-3 minutes.

Mice exposed to 13,500 parts per million of 1.1,1-trichloroethane became anaesthetized in an average time of 16.3 minutes (15.4-17.2) and died after an average of 595 minutes of exposure, Gehring, 1968 (124). Rats exposed to 5,000 parts per million of trichloroethane showed definite but mild narcotic effects within on hour while at 10,000 parts per million they showed decreased activity in 1-2 minutes with incoordination and difficulty in walking after 10 minutes and were semiconscious after three hours of exposure, Adams et al, 1950 (125). In

monkeys slight ataxia was produced after an hour of exposure at 5,000 parts per million of 1,1,1-trichloroethane.

#### 13.7.3.3 RENAL SYSTEM

Renal function in dogs exposed to 1,1,1-trichloroethane has shown changes as measured by PSP, glucose, and protein excretion data, but no history of pathological changes accompanied these findings, Klaasen et al, 1967 (126).

After intraperitoneal injection of 2.5 ml of 1,1,1-trichloroethane per kg of body weight given in olive oil swelling of the proximal convoluted renal tubule was reported in the 5 mice studied, Plaa et al, 1965 (37).

## 13.7.3.4 GASTROINTESTINAL TRACT

No reports of effects of 1,1,1-trichloroethane upon the gastrointestinal tract were found.

#### 13.7.3.5 LIVER

Summaries of many years of work on 3 chlorinated hydrocarbons have resulted in the following relative potency rankings in mice:

BPS retention, ED-50: trichloroethylene 1,1,1-trichloroethane, tetrachloroethylene

SGPT elevation, ED-50: 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene

24 hour LD-50: trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane.

When 1,1,1-trichloroethane is compared with 6 other halogenated solvents for the severity of liver damage produced when administered in doses within the lethal range (about LD-10) the elevation in transaminase is much lower for 1,1,1-trichloroethane than for the other halogenated solvents tested with the exception of trichloroethylene, Plaa, 1976 (74).

Because many blood clotting factors are produced by the liver and in addition have half lives often less than one day the measurement of such clotting factors can be a useful way of documenting the effects of chemicals upon the liver. In studies of 7 enzymes associated with blood clotting it was found that there were increases in activity in only 2 in rats given 1,650 mg of 1,1,1-trichloroethane per kg of body weight daily for 7 days. Both the NADPH-2-cytochrome C reductase and glutamate dehydrogenase activity of rat liver being significantly increased, Platt et al, 1969 (127).

The lowest concentration of 1,1,1-trichloroethane reported to have an effect upon the liver was a level of 250 parts per million which caused significant elevation of triglycerides levels in mice exposed for 4 and 13 weeks. The peak of triglyceride accumulation was rather broad and occurred approximately 7 weeks after the beginning of exposure. Recovery was partial and gradual over the 7 to 14 week interval following exposure. Although not as impressive as the necrosis caused by chloroform or carbon tetrachloride occasional necrotic hepatocytes associated with focal infiltrates of neutrophilic leukocytes were seen in these rat studies with 1,1,1-trichloroethane. These studies



also showed a dramatic increase in the number of microbodies after

4 to 14 weeks of exposure to 1,000 parts per million of 1,1,1-trichloroethane. Microbodies are described as membrane bound organelles that
are found in a large number of cell types. The functions of microbodies
may vary in different cell types depending on the enzymatic composition
of the cell. The microbody proliferation found in the mouse study
could be related to the accumulation of hepatic triglycerides or
possibly to a response of the hepatocyte to lipoperoxidation by
increasing the catalase content of the cytoplasm, McNutt et al, 1975 (128).
In contrast to these findings another study in mice continuously
exposed to 150 parts per million of 1,1,1-trichloroethane for 100 days
did not show any elevation of liver triglycerides but this effect was
found at 1,000 parts per million of 1,1,1-trichloroethane, MacEwan et al,
1974 (129).

# 13.7.3.6 CARDIOVASCULAR SYSTEM

A number of studies have shown depression in the contractility of the heart in animals in both isolated organ preparations and in the intact animal, Belej et al, (130), Aviado et al, 1975 (131), Herd et al, 1974 (132). While many questions still remain regarding the effects of 1,1,1-trichloroethane upon the cardiovascular system the studies reported to this date agree that hypotension commonly occurs with high 1,1,1-trichloroethane exposure. This effect has been reported at 6,250 parts per million of 1,1,1-trichloroethane in rabbits, 8,000 parts per million in dogs, 25,000 and 50,000 parts per million in humans,

Griffiths et al, 1972 (133), Dornette et al, 1960 (134).

1,1,1-trichloroethane has been shown to sensitize the heart to the effect of circulating epinephrine for a number of years and the compound has been used as a model for creating cardiac arrhythmias.

The minimal concentration of 1,1,1-trichloroethane that causes cardiac sensitization in the dog is 5,000 parts per million,

Reinhardt et al, 1973 (135). In a study of 1,1,1-trichloroethane as an anesthetic agent, Dornette et al, 1960 (134), a case of cardiac arrest was reported in 50 cases of anaesthesia and ECG changes consisting of depressed S-T segments, nodal rhythm change, and premature ventricular contractions were reported. Cardiac sensitization due to 1,1,1-trichloroethane can be prevented in mice with Propranolol and also with Reserpine. Both of these drugs block sympathetic activity but by different mechanisms.

The mechanism for cardiac arrhythmias seen with 1,1,1-trichloroethane is not clearly established but is believed by some investigators to be adrenergically mediated, Krantz et al, 1959 (136), and by another group of investigators to be a direct effect on the myocardium, Rennick et al, 1949 (137).

## 13.7.3.7 RESPIRATORY SYSTEM

Animals exposed to I,1,1-trichloroethane commonly show congestion of the lungs particularly in chronic or high level exposures. Pulmonary edema and congestion, however, are consistent with cardiovascular

Insufficiency and do not necessarily indicate a primary lung effect, Tsapko et al, 1972 (138), Horiguchi et al, 1971 (139).

#### 13.7.3.8 REPRODUCTIVE SYSTEM

In a study of the effect of 1,1,1-trichloroethane at a concentration of 875 parts per million on reproduction in mice and rats exposed for 7 hours daily from gestation day 6 to gestation day 15 no abnormalities were found in the per cent resorptions, average litter size, fetal body measurement, growth anomalies, soft tissue anomalies, skeletal anomalies, and microscopic examination. In the rats but not in the mice the absolute liver weight of the dams exceeded control levels but the relative liver weight (mg of liver/body weight) was normal, Schwetz et al, 1975 (24).

#### 13.7.3.9 ENDOCRINE SYSTEM

No reports of effects of 1,1,1-trichloroethane on the endocrine system have been found.

#### 13.7.3.10 EYES AND OTHER SENSE ORGANS

Instillation of 1,1,1-trichloroethane (5 % in corn oil) caused chemosis and hyperemia of the conjunctivas of rabbits, Krantz et al, 1959 (136). Similar findings in the eyes of rabbits were reported on the introduction of undiluted inhibited or uninhibited 1,1,1-trichloroethane, Torkelson et al. 1958 (142).

### 13.7.3.11 CARCINOGENICITY

A preliminary report has been published under the carcinogen bioassay and program resources of the National Cancer Institute (140). In this study rats and mice were given 1,1,1-trichloroethane by mouth at each of two dose levels 5 days a week for 78 weeks. The rats received 1,500 and 750 mg of 1,1,1-trichloroethane per kg of body weight while the mice received doses increasing with their body weight gain, the doses averaging 5,615 and 2,807 mg of 1,1,1-trichloroethane per kg of body weight. The solvent used in these studies was technical grade, containing 95 % 1,1,1-trichloroethane, 3 % paradioxane and 2 % of minor impurities and inhibitors.

The survival time in weeks was significantly decreased in the l,l,l-trichloroethane treated animals compared with the control animals. Four neoplasms occurred in the test groups of rats but each type of neoplasm encountered had been previously found as a spontaneous lesion in this strain of rat. No relationship to the exposure to l,l,l-trichloroethane was evident either in the types of tumors found or in the incidence of tumors.

In the mice, all the tumors found in the exposed group were also seen in the control group and there was no statistically significant difference in the numbers of tumors encountered. The National Cancer Institute Report concludes that the neoplasms seen were not believed to be attributable to 1,1,1-trichloroethane exposure. It is understood that replications of these tests are now underway or planned.

#### 13.7.3.12 MUTAGENICITY

No reports on the mutagenicity of 1,1,1-trichloroethane were found but from the very small percentage of the material that is metabolized and the fact that the metabolic pathway believed to be taken by 1,1,1-trichloroethane does not include transformation to an epoxide which is one of the postulated mechanisms for producing mutagenicity.

## 13.7.3.13 TERATOGENICITY

In the study by Schwetz referred to previously the authors concluded that there were no teratogenic effects in either rats or mice. But abnormalities did occur in the litters of the exposed rats and mice. These abnormalities were not found in the litters from control mothers. Significant subcutaneous edema, delayed ossification in the skull and the presence of split sternebrae were found in pups born to mothers exposed to tetrachloroethylene. The results of these tests raises the possibility of 1,1,1-trichloroethane having a low grade mutagenic effect and the replication of these tests would be desirable. No other reproductive studies or studies of mutagenicity involving exposure to 1,1,1-trichloroethane were found.

## 13.7.3.14 FACTORS AFFECTING TOXICITY

#### 13.7.3.14.1 TOLERANCE

No reports of unusual tolerance to 1,1,1-trichloroethane were found.

## 13.7.3.14.2 SUSCEPTIBILITY

As mentioned under the section on Cardiovascular effects of 1,1,1-trichloroethane high circulating levels of epinephrine in the presence of the solvent may result in cardiac arrhythmias and in some cases sudden death.

The giving of ethyl alcohol to rats increases the hepatotoxicity of 1,1,1-trichloroethane. BSP retention being significantly higher in the alcohol pre-treated rats than in the control rats given only 1,1,1-trichloroethane. The alcohol was given at a dose of 5 mg/kg on each of three days before the intraperitoneal injection of 2.5 to 2.75 ml of trichloroethane/kg of body weight, Klassen et al, 1967 (126).

Another example of the interaction of chemicals with the biological effects of 1,1,1-trichloroethane is represented by the difference between using the pure solvent and commercial material which contains a variety of inhibitors. These inhibitors are of three types:

- 0xygen containing compounds and nitroalkanes which inhibit
  or control the removal of chlorine by the more reactive methyls
  with the formation of the corresponding anhydrous methyl chloride
  which are often very reactive catalysts.
- 2. Since the inhibitors are not 100 % effective hydrogen chloride is generated as a result of the formation of the dehydrochlorination catalysts. Acetic acid and hydrogen chloride are also generated as a result of the removal of chlorine from 1,1,1-trichloroethane by the action of water. For this reason acid scavengers (usually alpha epoxides) are also added to 1,1,1-trichloroethane for use in commerce.



 To prevent breakdown of the solvent at elevated temperatures formal stabilizers, usually aromatic or aliphatic hydrocarbons are used.

Analysis of commercial samples of 1,1,1-trichloroethane has given the following ranges of stabilizer concentrations.

Stabilizer	Approximate Volume %
Nitromethane	0.4 - 1.8
Secondary Butyl Alcohol	0.2 - 0.3
Isobutyl Alcohol	1.0 - 1.4
Butylene Oxide	0.4 - 0.8
Dioxane	1.0 - 1.4
Methylethylketone	1.0 - 1.4
Dimethoxymethane	4.0 - 4.5
Toluene	1.0 - 1.4
Tetrahydrofuran	1.0 - 3.0

The majority of inhibitors are more toxic than 1,1,1-trichloroethane although the quantities present in the work place atmosphere would be small. Since 1,4 dioxane, which is a highly efficient inhibitor and has been used at the 3-4 % level in commercially stabilized 1,1,1-trichloroethane, has been designated as a carcinogen, and there is no standard in the United States for a safe exposure level to a chemical defined as a carcinogen, this raises a problem with the use of this inhibitor in 1,1,1-trichloroethane commercial solvents, Llewellyn, 1972 (141). The presence of inhibitors in commercial solvents draws attention to the need to carefully define the materials used in toxicity

testing, Torkelson et al. 1958 (142).

The chlorinated hydrocarbon solvents can be broadly divided into two groups: those like carbon tetrachloride and chloroform which are metabolized with the production of free radical intermediates and those like 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene which are metabolized to alcohols and acids. The toxicity of the former is potentiated by microsomal enzyme inducers such as phenobarbital while the toxicity of the latter group is not potentiated by enzyme inducers. Cornish et al, 1973 (64). It appears from other experiments that 1,1,1-trichloroethane can itself act as an inducer of microsomal enzymes. This effect has been suggested by the decrease in sleeping time produced by phenobarbital and hexobarbital when the animals (rats and mice) were pre-exposed to 2,500 to 3,000 parts per million of 1,1,1-trichloroethane for 24 hours. Fuller et al, 1970 (144).

#### 13.7.3.14.3 AGE

No clear effect of age on the toxicity of 1,1,1-trichloroethane was found in published reports.

## 13.7.3.14.4 SEX

No reports of differences in the toxicity of 1,1,1-trichloroethane in male and female animals were found, but in a number of investigations animals of only one sex were used.

#### 13.7.3.14.5 SEASONAL VARIATIONS

No reports of changes in toxicity based on seasonal variations were found.

#### 13.7.3.14.6 NUTRITION

No reports of the effects of nutrition on the toxicity of 1,1,1-trichloroethane were found.

### 13.7.3.14.7 HEALTH OF THE INDIVIDUAL

In rats made diabetic with alloxan the effect of intraperitoneal insection of 1,1,1-trichloroethane (1.0 ml/kg) on the liver was to increase SGPT and triglycerides levels significantly over those in control animals, Hanasono et al, 1975 (143).

#### 13.7.4 HUMAN EXPERIENCE

#### 13.7.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

The use of 1,1,1-trichloroethane as an anaesthetic agent was investigated during the last century and it was found effective as a depressant of the central nervous system, but it was not as potent as other available agents and its relative lack of effectiveness resulted in the discontinuance of the use of 1,1,1-trichloroethane as an anaesthetic agent, Dornette et al, 1960 (134), Von Oettingen, 1964 (2).

No effects of 1,1,1-trichloroethane on balance and co-ordination tests were found in humans exposed to 500 parts per million for three hours, but four out of five subjects showed deleterious effects on these tests when exposed to the same level but for 6-1/2 to 7 hours, Stewart et al, 1969 (145). In an experiment in which the concentration

of 1,1,1-trichloroethane was increased rapidly from 0 to 2,650 parts per million over a period of 15 minutes, one subject became lightheaded at 2,600 parts per million, while two subjects could not stand and three others were very lightheaded. A total of seven subjects were used in this experiment, and while one subject showed no unsteadiness on standing with his eyes closed the other six subjects showed varying degrees of unsteadiness. These six subjects regained their equilibrium within five minutes after the cessation of exposure. Lightheadedness was reported to continue for five hours after the end of exposure in the five subjects who became lightheaded during the experiment. The feeling of malaise and tiredness for several hours after exposure to 1,1,1-trichloroethane appears to characteristic of exposure to relatively high concentrations of this solvent, Stewart et al, 1961 (120).

In tests of psychophysiological performance in six students aged 20 to 23 years of age exposed to 1,1,1-trichloroethane at 350 and 450 parts per million both at rest and during exercise the only abnormal finding was a decrease in perceptive capability at 450 parts per million, Salvini et al, 1971 (146), (147).

In experimental tests using twelve subjects exposed to 250, 350, 450 and 550 parts per million of 1,1,1-trichloroethane during four continuous 30-minute periods the subjects performed tests of perceptual speed and tests of simple reaction time, choice reaction time and manual dexterity. Statistically significant performance differences between experimental and control conditions were obtained for all tests with exposures of 350 parts per million or more (147).



Few epidemiological studies of the effects of chronic exposure to 1,1,1-trichloroethane have been reported, and those which have been reported are seldom adequate in the exposure information available or in being able to specify what other exposures in addition to 1,1,1-trichloroethane may have also taken place.

In a study of matched pairs of workers in adjacent textile plants, one of which employed 1,1,1-trichloroethane as a solvent and the other plant (the control plant) did not, the range of concentration of 1,1,1-trichloroethane was 11 to 838 parts per million, with a mean of 115 parts per million. The duration of exposure was up to six years, with an average length of exposure of less than one year. The control group had minimal exposure to solvents and none to chlorinated solvents. Measurements were made of the participants' height, weight, blood pressure, liver function tests, electrocardiograms and hematology. Comparison of the exposed and control group data showed no statistically significant difference except for SGPT and albumin. Although the period of exposure for many of the workers was not very great and the range of exposure concentrations was not very wide, this study is one of the few available at an exposure level close to the threshold limit value (147).

In a brief report mainly dealing with analytical methods for halogenated hydrocarbons brief reference is made to symptoms among Italian workers when 1,1,1-trichloroethane was introduced as a solvent. The concentration of 1,1,1-trichloroethane found in the workroom air was reported to be 250 parts per million (147).

Three cases were reported in 1969 of deaths due to inhalation of 1,1,1-trichloroethane at work. A 20-year-old died after working with "paint remover" for an unknown time. 2.7 mg of 1,1,1-trichloroethane per 100 grams of brain tissue were found at autopsy.

A 17-year-old died 3-3/4 hours after cleaning metal parts in a closed area. 0.32 mg of 1,1,1-trichloroethane were found per 100 grams of brain tissue.

A 24-year-old was found dead two hours after cleaning metal parts, and at autopsy the liver showed prominent fatty changes in the tissue concentration of 1,1,1-trichloroethane was 9.3 mg per 100 grams of brain tissue, Stahl et al, 1969 (148).

A 47-year-old male accidentally drank an estimated 670 mg per kg of body weight of 1,1,1-trichloroethane. The patient immediately experienced a burning sensation in the upper gastrointestinal tract.

Nausea occurred at 30 minutes and diarrhea with vomiting occurred at one hour. Some hours later the urine showed 1+ protein, a tract of glucose and some red cells, indicating kidney damage. Symptoms decreased after six hours and the man was asymptomatic after 12 hours. The serum bilirubin was elevated when performed 50 hours later, but a large number of kidney and liver function tests were found to be normal, Stewart et al, 1966 (149).

#### 13.7.4.2 HEMATOPOIETIC SYSTEM

No reports of effects of 1,1,1-trichloroethane on the hematopoietic system have been found.



### 13.7.4.3 NERVOUS SYSTEM

l,l,l-trichloroethane is a central nervous system depressant, and from information previously referred to it appears that this effect as detected by complaints of lightheadedness and evidence of muscular incoordination may occur at levels above 250 parts per million.

A clinical, neurophysiological and behavioural study of 22 female workers in a factory in which 1,1,1-trichloroethane was the only solvent used was carried out and the results compared with a group of workers not exposed to the solvent. The mean length of exposure was 6.7 years and the exposure levels ranged from 110 to 345 parts per million. No significant difference was observed between exposed and unexposed females with respect to clinical features, maximum motor conduction velocity, conduction velocity of slow fibres and psychometric data. The most frequent complaints of the workers were of the "neurotic" type, with a slightly higher but not significant difference in the exposed group. These results are in agreement with the other data presented that within the context of the working situation described, neurophysiological effects are not detectible in workers at levels below about 350 ppm, Maroni et al, 1977 (150).

### 13.7.4.4 RENAL SYSTEM

As referred to above, exposure to 1,1,1-trichloroethane

(670 mg/kg) can produce minimal kidney injury in man, as shown by the

presence of red cells and protein in the urine.

#### 13.7.4.5 GASTROINTESTINAL TRACT

Apart from a burning sensation and nausea on accidental ingestion, no other reports of effects of 1,1,1-trichloroethane on the gastrointestinal tract have been found.

#### 13.7.4.6 LIVER

In patients undergoing surgery where 1,1,1-trichloroethane was used as an anaesthetic agent, two out of five patients showed slight increases in serum transaminase, Dornett et al, 1960 (134). In one study seven subjects were exposed for 15 minutes at a concentration of 1,1,1-trichloroethane rising from zero to 2,650 parts per million. Two out of the seven subjects in this study showed positive urinary urobilinogen, Stewart et al, 1961 (120). A similar elevation in urinary urobilinogen was found in a subject following a 20-minute exposure at 900 parts per million of 1,1,1-trichloroethane, Stewart et al, 1961 (120).

#### 13.7.4.7 CARDIOVASCULAR SYSTEM

During the use of 1,1,1-trichloroethane in 50 cases of human anaesthesia previously referred to, Dornette et al, 1960 (134), the blood pressure was depressed but no consistent changes in electrocardiographic patterns were found. The changes observed in the electrocardiogram included premature ventricular contractions and depressed S-T segments. There was one case of cardiac arrest but it was not known if the anaesthesia contributed to this event.



In a severe case of abuse of 1,1,1-trichloroethane by a young seaman progressive hypotension and bradycardia with several instances of cardiac arrest preceded his death 24 hours after the initial incident.

As referred to in the sections dealing with the effect of 1,1,1-trichloroethane on the cardiovascular system of animals, sensitization to circulating epinephrine is thought to account for the cases of sudden death which have occurred both in animals and in humans exposed to 1,1,1-trichloroethane. In a survey of 110 cases of sudden death associated with the abuse of various solvents, 18 of the 110 cases were due to exposure of 1,1,1-trichloroethane, Bass, 1970 (151), Hatfield et al, 1970 (152), Kleinfeld et al, 1966 (153).

In those cases of sudden death while exposed to 1,1,1-trichloroethane it is difficult to prove that cardiac arrhythmias are responsible, but the circumstances surrounding the deaths are consistent with such a mechanism and the deaths have usually been associated with exercise or a degree of excitement, as in the sniffing deaths, or both unusual exertion and excitement were present together as in some of the situations in industry where fellow workers rushed to the aid of a person overcome by solvent vapors.

### 13.7.4.8 RESPIRATORY SYSTEM

No reports of adverse effects of 1,1,1-trichloroethane on the human respiratory system have been found.

### 13.7.4.9 REPRODUCTIVE SYSTEM

No reports of the effects of 1,1,1-trichloroethane upon the human reproductive system have been found.

# 13.7.4.10 ENDOCRINE SYSTEM

No reports of the effects of 1,1,1-trichloroethane on the human endocrine system have been found.

### 13.7.4.11 EYES AND OTHER SENSE ORGANS

1,1,1-trichloroethane is irritating to mucous membranes but no reports of specific effects on eyes or other sense organs have been found.

#### 13.7.4.12 CARCINOGENICITY

No reports suggestive of carcinogenicity in humans due to exposure to 1,1,1-trichloroethane have been found.

#### 13.7.4.13 TERATOGENICITY

No reports of teratogenic effects of 1,1,1-trichloroethane in humans have been found.

#### 13.7.4.14 FACTORS AFFECTING HUMAN RESPONSE

Although the animal studies referred to previously might suggest a number of factors (eg alcohol and sedatives) that might influence the toxicity of 1,1,1-trichloroethane, no documentation of such effects has been found in humans.



# 13.8 1,1,2,2-TETRACHLOROETHANE

### 13.8.1 SUMMARY OF BIOLOGICAL INFORMATION

A strong central nervous system depressant with persistent neurological symptoms often reported after end of exposure with tremor of hands and vertigo. Liver damage and jaundice in humans and animals is also prominent feature and occurs at low levels 2-200 ppm.

Occupational exposure limit 1 ppm (TWA).

Toxicity Rating: [A]

### Toxicity to Animals

Test	Rating
Acute	High
Chronic	High

### Toxicity to Man

Test	Rating
Experimental	High
Epidemiological	Hiah

# 13.8.2 ANIMAL EXPERIMENTAL STUDIES

Tetrachloroethane has a local irritating effect similar to trichloroethane although somewhat stronger. It is one of the most poisonous of the chlorinated hydrocarbons and is absorbed readily through the lungs and skin. Being fat soluble tetrachloroethane is found in body fat, the brain, and to a lesser extent in liver, blood and kidneys after exposure. Excretion occurs chiefly through the lungs but also to a much lesser extent through the kidneys. On acute exposure



animals show signs due to the irritation of the compound with tearing and sneezing followed by trembling, stiffness in the legs and paralysis. Death may occur at once or may be delayed for several days. Fatty degeneration of the liver and kidneys has been observed. The fatal concentration for mice is reported to be about 30 mg/litre while 4.3 mg/litre causes prostration after about 80 minutes of inhalation in the mouse and 7 to 19 mg/litre causes narcosis in mice after 20 minutes.

### 13.8.3 HUMAN EXPERIENCE

Because of its toxicity tetrachloroethane is little used in industry and its use as a lacquer solvent which resulted in illness in a number of workers caused its use for that and other similar purposes to be discontinued in most countries prior to 1936. Chronic exposure has been reported to cause tremors, headache, and excessive sweating. A number of fatal cases of tetrachloroethane poisoning following both inhalation of the vapor and swallowing of the liquid have been reported. In severe cases vomiting and jaundice due to severe fatty degeneration of the liver have been reported.

## 13.9 VINYLIDENE CHLORIDE

Because there is less toxicological information available on vinylidene chloride the format used in the other documents in the presentation of the information relative to health effects will not be used and a summary form substituted.

### 13.9.1 SUMMARY OF BIOLOGICAL INFORMATION

An irritant to mucus membranes with its main impact on the liver. Intermittant exposure of rats (6 hrs/day, 5 days/week for 18 months) showed minimal changes in the liver at 25-75 parts per million. Continuous 90 day exposure at 15-5 parts per million produced appreciable mortality among rats, guinea pigs and monkeys. Vinylidene chloride is mutagenic in bacteria. Kidney carcinomata have been reported in male mice at 25 parts per million vinylidene chloride for 1 year but no such tumors were found in male or female mice exposed at 10 parts per million for one year.

### Toxicity Rating: [B]

No satisfactory human exposure data available upon which an assessment of the hazard of vinylidene chloride to human health could be made.

#### Toxicity to Animals

Test	Rating
Acute	Moderate
Chronic	High

#### Toxicity to Man

<u>Tes t</u>	Rating
Experimental	No Data
Epidemiological	No Data



#### 13.9.2 ANIMAL STUDIES

The acute toxicity of vinylidene chloride to rats as measured by the LD-50 test has been reported as 1,550 parts per million for a 24 hour exposure with a range from 1520 to 1581 parts per million. The 4 hour LD-50 value is reported as between 10,000 and 15,000 parts per million in rats fed a normal diet and 500 to 2500 parts per million in fasted rats. Vinylidene chloride is irritating to animals as shown by blinking, lacrimation, nasal irritation, roughened coat, excessive salivation, accelerated respiration, followed by gasping, tremors, convulsions, incoordination, prostration, narcosis and death. After a 4 hour exposure to 200 parts per million of vinylidene chloride the hepatic pathological changes consisted of midzonal necrosis, damaged parenchyma, thrombus and a few inflammatory cells, but no fatty infiltration (154). When rats are exposed for longer periods the irritating properties of vinylidene chloride are evident at 200 parts per million daily for 20 days. Rats exposed to 500 parts per million vinylidene chloride showed symptoms of nasal irritation and retarded weight gain. Histological examination revealed liver cell degeneration (155). When rabbits, rats, dogs, monkeys and guinea pigs were exposed to 100 parts per million for 8 hours a day, 5 days a week for a period of 6 weeks, the rabbits and monkeys lost weight but no animals died (156). When continuous rather than periodic exposures were used 7 out of 15 guinea pigs died between the 4th and 9th day of exposure to 67 parts per million while 3 out of 9 monkeys died on days 26, 60 and 64 of the 90 day exposure (156). The striking difference between the results of

continuous exposure versus periodic exposure is demonstrated in a 90 day exposure to 25 parts per million during which 3 out of 15 guinea pigs died between the 3rd and 6th day of exposure and 2 out of 3 monkeys on days 39 and 47. At the still lower exposure level of 15 parts per million 3 out of 15 guinea pigs died on the 3rd and 4th days of exposure. While even at 5 parts per million 2 out of 45 rats, 2 out of 45 guinea pigs, and 1 out of 21 monkeys died (156). In contrast to these findings rats exposed to 25 to 75 parts per million, 6 hours a day, 5 days a week for up to 18 months, showed only minimal microscopic changes in the liver and no other significant findings (157).

### 13.9.2.1 LIVER

Within 2 to 4 hours of exposure to 2000 parts per million of vinylidene chloride hemorrhage and necrosis can be observed in liver sections of fasted rats. Microscopic examination of the liver shows the liver injury due to vinylidene chloride to first appear as vacuolation in the cytoplasm of the hepatocytes. Such changes are found in rats exposed to 25 to 75 parts per million of vinylidene chloride for 30 or 90 days. The incidence of liver injury is dose related and increases with the duration of the exposure. At a dose of 800 mg per kilogram of body weight of vinylidene chloride the amount of neutral fat within the liver is almost double that of control animals (158). Compounds which induce liver enzymes such as phenobarbital and 3-methylcholanthrene increase the toxicity of vinylidene chloride. This



is in contrast to the effect of these enzyme inducing agents on the toxicity of carbon tetrachloride where 3-methylcholanthrene protects against the effects of carbon tetrachloride, whereas phenobarbital accentuates the toxicity of this solvent (159). Glutathione depletion renders animals more sensitive to vinylidene chloride toxicity as shown by liver damage. This may be the mechanism for the greater susceptibility for fasted animals to vinylidene chloride since glutathione concentrations fall during fasting. Fasted rats show a threshold for vinylidene chloride toxicity, 100 parts per million being without serious effect on the liver while 150 parts per million causes a significant elevation of serum alanine ketaglutarate transaminase and at 200 parts per million the concentration is fatal to some rats. In contrast, normally fed rats exposed at 2000 parts per million showed some evidence of liver injury but no deaths (158).

### 13.9.2.2 KIDNEY

Renal changes thought to be a direct result of exposure to vinylidene chloride have been reported. Histological examination of the kidneys from rats exposed to vinylidene chloride showed nuclear hypertrophy of the tubular epithelium (156).

#### 13.9.2.3 NERVOUS SYSTEM

Vinylidene chloride is a central nervous system depressant and high concentrations can produce a strong narcotic effect with unconsciousness (160).

# 13.9.2.4 CARDIOVASCULAR SYSTEM

Vinylidene chloride has been shown to sensitize the hearts of laboratory rats to circulating epinephrine. Pre-treatment with phenobarbital enhances the cardiac sensitization to vinylidene chloride suggesting that it is a metabolite of vinylidene chloride that sensitizes the heart rather than vinylidene chloride itself (161).

## 13.9.2.5 MUTAGENICITY

Vinylidene chloride induces point mutation in the histidine auxotroph strains of Salmonella typhimurium and TA1530 and TA100 when tested in the presence of rat or mouse liver in vitro. In this test its mutagenic activity was greater than that of vinyl chloride monomer. It has been postulated that 1,1-dichloroethylene oxide may be a primary reactive metabolite of vinylidene chloride. It is also considered possible that partial dechlorination of vinylidene chloride by microsomal enzymes results in vinyl chloride and its metabolic products (162). Vinylidene chloride has also been found to be mutagenic when tested in a metabolizing in vitro system with E. coli Kl2. In contrast to the results in Salmonella typhimurium the mutagenicity of vinyl chloride monomer was several times higher than that of vinylidene chloride when tested in E. coli (back-mutation system) (186). While early reports (1974) suggested that inhaled vinylidene chloride might be carcinogenic to rats at high concentrations, later findings indicated that the tumor incidence in the rats was similar to the tumor incidence in the controls (163). It has been reported that male mice exposed to 25 parts

per million of vinylidene chloride for one year developed kidney carcinomas whereas female mice exposed for the same length of time to the same concentrations did not develop kidney tumors. At a concentration of 10 parts per million of vinylidene chloride neither male nor female mice developed tumors. In tests using rats and hamsters exposed to vinylidene chloride no evidence of carcinogenicity was found (163). A one year inhalation study of vinylidene chloride using mice and rats showed that at 55 parts per million of vinylidene chloride for 6 hours a day, 5 days a week, two male mice and one female mouse developed hemangiosarcomata while no such tumors were found in the livers of control mice. One rat exposed to vinylidene chloride developed a hemangiosarcoma of a mesenteric lymph node and another exposed rat developed a subcutaneous hemangiosarcoma. No hemangiosarcomas were observed in control rats (163). The results of these exposures are not conclusive since the incidence of hemangiosarcomas observed in the rats and mice was too low to be considered proof of carcinogenicity.

#### 13.9.3 HUMAN EXPERIENCE

No reports of humans exposed solely to vinylidene chloride were found.

Reports of mixed exposures in which the vinylidene chloride was present

in low concentrations are difficult to interpret.

# 13.10. TRICHLOROETHYLENE

# 13.10.1 SUMMARY OF BIOLOGICAL INFORMATION

Eye and nose irritant. Central nervous system depressant. Cancer of the liver produced in rats given very high levels of compound. No cases of cancer due to compound have been reported in man but no detailed epidemiological surveys have been made. Sudden deaths have been reported in workers exposed to "high" levels when undertaking sudden or heavy physical exertion. This effect is thought to be due to cardiac arrhythmias.

Not a proven carcinogen for man. No change has yet been made in occupational limit of 100 ppm (TWA).

Toxicity Rating:

[B]

Toxicity to Animals

<u>Test</u> <u>Rating</u>

Acute Low

Chronic Low

Toxicity to Man

Test Rating

Experimental Low

Epidemiological Moderate

#### 13.10.2 METABOLISM

Trichloroethylene undergoes three major metabolic transformations in the body: (1) oxidation to chloral hydrate in the microsomal fraction of the liver cells; (2) reduction to trichloroethanol; and (3) oxidation to trichloroacetaldehyde.



Minor trichloroethylene metabolites have also been reported but there is no general agreement among investigators as to which compounds should be considered the true minor metabolites. At this time it appears that chloral hydrate and monochloroacetic acid are probably the only true minor trichloroethylene metabolites.

The biological half-life of trichloroethylene has been studied by a great number of investigators and the mean value has been calculated as about 41 hours in human subjects, 1keda et al, 1973 (165). The biological half-life to which these investigators refer is the half-life of the metabolites of trichloroethylene in the urine of human subjects exposed to trichloroethylene vapor. The biological half-life of metabolites in the blood of human subjects is about 12 hours, Erple et al, 1972 (166), Muller et al, 1974 (167). The existence of an epoxide intermediate in the metabolism of trichloroethylene has been suspected for some years and the formation of such epoxides is now recognized as an obligatory intermediate step in the metabolism of olefins by hepatic microsomal mixed-function oxidases, Maynert et al, 1970 (168). The formation of metabolites such as trichloroethanol and trichloroacetic acid implies rearrangement of the transient trichloroethylene oxide intermediate into chloral hydrate. These steps have been confirmed in vitro and in some cases in vivo, Bonse et al, 1975 (169), Byington et al, 1965 (170).

Trichloroethanol is most often conjugated with glucuronic acid before being excreted in the urine, and as with most detoxification reactions this conjugation takes place mainly in the liver.

#### 13.10.2.1 ABSORPTION

Trichloroethylene may be absorbed by inhalation, ingestion and through the skin. Inhalation is by far the most important route and absorption proceeds rapidly during the first few minutes of exposure and then decreases until equilibrium with the blood is achieved or the exposure ends.

Numerous cases of oral ingestion of trichloroethylene have demonstrated that the solvent passes across the gastrointestinal mucosa with ease.

Trichloroethylene is not absorbed through the skin in significant quantities, however, some absorption can be demonstrated. Stewart et al, 1964 (171).

#### 13.10.2.2 DISTRIBUTION AND RETENTION

Trichloroethylene after absorption is readily taken up by the blood and disappears equally rapidly. Because of its high fat solubility that fraction of trichloroethylene that is not immediately metabolized may be retained in fatty tissues. In obese subjects, after inhalation of trichloroethylene the amount of the solvent was considerably lower in venous than in arterial blood. This fact suggests that because of the high lipid solubility of trichloroethylene, it can be readily extracted from the blood by fatty tissues, Clayton et al, 1962 (172).

In a subject exposed to 211 parts per million of trichloroethylene



for 190 minutes the concentration of the solvent in the blood after two hours of exposure was 6 parts per million while 20 minutes after the end of the exposure the blood level had fallen to 1 part per million, Stewart et al, 1962 (173). The metabolites of trichloroethylene, however, can be detected for much longer periods after the end of exposure to the solvent. After a single exposure to 50 parts per million of trichloroethylene, trichloroethanol was detectable in the blood of the human subject four days after the exposure, Ertle et al, 1972 (166).

### 13.10.2.3 ELIMINATION

Following absorption of trichloroethylene the majority of the solvent is exhaled unchanged in the breath. The concentration in the breath follows an exponential decay curve. The metabolites trichloroethanol and trichloroacetic acid have quite different biological half-lives in humans. Trichloroethanol has a half-life of 13 hours compared with a value of 50 to 99 hours for trichloroacetic acid, Muller et al, 1974 (167). When radio-labelled trichloroethylene is given by mouth to rats the majority (72-85 %) of the dose is excreted through the lungs leaving the rest to be excreted in the urine (11-21 %), Daniel, 1963 (174). When the dose of trichloroethylene is increased the proportion of the solvent excreted through the lungs increases and the metabolites in the urine account for a smaller proportion of the total excretion. This finding suggests that the metabolic pathways may be a limiting factor in trichloroethylene excretion.

# 13.10.3 ANIMAL EXPERIMENTAL STUDIES

## 13.10.3.1 HEMATOPOIETIC SYSTEM

No reports of effects of trichloroethylene on the hematopoietic system of animals were found.

#### 13.10.3.2 NERVOUS SYSTEM

Trichloroethylene is a central nervous system depressant. Rats exposed for 6 hours to 400, 800 and 1600 parts per million of trichloroethylene showed no effect at 400 parts per million as tested by a 4 hour swimming test. Exposure to 800 parts per million caused a decrease in motor performance but normal activity was regained after 1 hour, whereas exposure to 1600 parts per million impaired motor activity for 80 minutes, Grandjean, 1963 (175).

Exposure of rats to 360-420 parts per million of trichloroethylene 8 hours a day for 5 days a week with a total duration of 46 weeks caused no behavioral abnormalities in the animals, Baettig et al, 1963 (176).

#### 13.10.3.3 RENAL SYSTEM

Cytotoxicity has been reported in the liver and kidneys following exposure of dogs to 1.5 % volume/volume trichloroethylene. At this level the dogs experience anaesthesia, Kiseleva et al, 1971 (177). In rabbits injected with 35 to 55 grams of trichloroethylene daily for 55 to 100 days there were two deaths, both of which were attributed to renal failure, Bartonicek et al, 1959 (178).

Mice injected with 0.6 mg per kg of body weight trichloroethylene



showed no change in renal function as measured by PSP excretion, and urinary sugar excretion. Histopathological examination of the kidneys was reported to be normal, Plaa et al, 1965 (37).

### 13.10.3.4 GASTROINTESTINAL TRACT

No reports of effects of trichloroethylene on the gastrointestinal tract were found.

### 13.10.3.5 LIVER

Because of the lack of verification by later experiments the early investigations of trichloroethylene effects on the liver in which some degree of liver damage was found may be due to impurities in the trichloroethylene used. Recent experiments using purified trichloroethylene have either shown no effect or the results have been inconclusive.

Rats exposed to trichloroethylene for 30 minutes a day for 120 days showed liver damage resulting in histological changes, decreased total serum proteins and albumin levels, and increased alpha, beta and gamma-globulins and cholesterol, Waters et al, 1977 (179).

In studies of the comparative hepatic toxicity of the number of chlorinated hydrocarbon solvents, it was shown, Plaa, 1976 (74), that when 6 halogenated hydrocarbons were ranked according to their relative potencies then the 24 hour LD-50 was a poor index of hepatotoxicity. If, however, instead of using the LD-50 the BSP retention or SGPT elevation is used, the relative potencies for these measurements agree quite well with the known hepatotoxic potencies of the halogenated nydrocarbons

based on industrial experience.

When SGPT elevation is used as the measure of hepatic dysfunction, carbon tetrachloride is distinctly more toxic than the other chlorinated hydrocarbons tested (1,1,2-trichloroethane, chloroform, 1,1,1-trichloroethylene, tetrachloroethylene) and trichloroethylene ranks fifth out of the six solvents tested. Similarly with BSP retention carbon tetrachloride is the most toxic to the mouse liver and trichloroethylene ranks fourth of the six compounds tested. No liver damage was found in rats following a single 4 hour exposure to 3,200 parts per million of trichloroethylene as measured by serum ornithine carbamoyl transferase (SOCT) activity and histological examination, Kylin et al, 1963 (39). Rats injected intraperitoneally every second day with trichloroethylene for a total of 40 doses (0.5 mg per kg for 3 doses and 1.5 mg per kg for 37 doses), showed no significant changes in the liver or levels of blood lipids, phospholipids, total cholesterol, triglycerides, free fatty acids, glycogen or glucose, Ikeda et al, 1969 (180).

On balance the effect of trichloroethylene upon the liver appears to be mild in comparison with other chlorinated hydrocarbon solvents, both based on experimental results and experience in industry.

# 13.10.3.6 CARDIOVASCULAR SYSTEM

The most common effect of tricnloroethylene upon the heart is the production of cardiac arrhythmias. This effect is believed to be due to the sensitization of the heart to circulating epinephrine. This phenomenon can be demonstrated in dogs at trichloroethylene levels of



0.5 % and higher, Reinhardt et al, 1973 (135).

Trichloroethylene also causes depression of myocardial contractility and this effect is apparent at levels of 500 parts per million and above, Aviado et al, 1976 (181).

#### 13.10.3.7 RESPIRATORY SYSTEM

The toxic effects of trichloroethylene upon the lung are secondary to its central depression of respiration.

#### 13.10.3.8 REPRODUCTIVE SYSTEM

In a study comparing the effects of chlorinated hydrocarbon solvents on pregnant mice and rats (trichloroethylene, perchloroethylene, methylchloroform and methylene chloride) the solvents had little effect on embryonal and fetal development at the levels tested. None of the solvents were teratogenic in either species. 300 parts per million of trichloroethylene was the only level tested of this solvent in this set of experiments, Schwetz et al, 1975 (24).

No other adequately documented effects of trichloroethylene on reproduction were found.

#### 13.10.3.9 ENDOCRINE SYSTEM

No reports of effects of trichloroethylene upon the endocrine system were found.

#### 13.10.3.10 EYES AND OTHER SENSE ORGANS

Trichloroethylene is irritating to the eyes, mucous membranes and upper portion of the respiratory tract. No other reports of the effects

of trichloroethylene on the eye were found.

# 13.10.3.11 CARCINOGENICITY

On March 22, 1975 the National Cancer Institute in the United States issued a memorandum warning that preliminary tests in mice implicated trichloroethylene as the cause of hepatocellular carcinoma with some metastases. These results were contrary to those of long-term studies reported to that date but none of the studies were maintained for as long as the National Cancer Institute studies nor were as many animals used, Seifter, 1944 (182), Adams et al, 1951 (183), Mosinger et al, 1955 (184), Rudali, 1967 (185).

The National Cancer Institute study involved gastric intubation of trichloroethylene into male and female Osborne-Mendel rats and B6 C3 F1 mice. In the rats the dose levels were 1,097 and 549 mg of trichloroethylene per kg of body weight dissolved in corn oil and administered five times a week for 78 weeks. All surviving rats were sacrificed at 110 weeks and subjected to extensive pathological examination. Chronic respiratory disease occurred in most rats regardless of treatment group or sex. The only treatment-related lesion was chronic neuropathy present in rats of both sexes at high and low dose levels. The experimental doses of trichloroethylene used amounted to approximately one-fifth to one-tenth of the LD-50 value. Matched control rats showed a 20 % incidence of hepatocellular carcinoma in males and a 35 % incidence in females. Both values are greater than the occurrence of hepatocellular carcinoma in trichloroethylene treated

males and females. The decreased rate of hepatocellular carcinoma with increased dose of trichloroethylene may be explained by the greater number of deaths caused by the toxic effects of trichloroethylene before sufficient time had elapsed for tumors to develop.

The mice were subjected to a similar experimental protocol, receiving trichloroethylene by gastric intubation at dose levels of 2339 and 1169 mg of trichloroethylene per kg of body weight for males and 1739 and 869 mg of trichloroethylene per kg of body weight for females 5 times a week for 78 weeks. Surviving mice were sacrificed at 90 weeks and subjected to pathological examination. The mortality rate in matched control male mice was higher than in the trichloroethylene treated mice. 64 % of the males fed trichloroethylene at the high dose level and 52 % fed at the lower dose level developed hepatocellular carcinoma. For females the incidence was 23 and 8 %respectively. These experiments are suggestive that trichloroethylene is a carcinogen in mice but the results are not conclusive and it is of interest that the International Agency for Research on Cancer (IARC) in evaluating the carcinogenic potential of trichloroethylene presented only pre-publication results from the U\$ National Cancer Institute Study and in the absence of any confirmatory epidemiological data drew no conclusions.

#### 13.10.3.12 MUTAGENICITY

Trichloroethylene at a concentration of 3.3 millimoles in the presence of a metabolic activating microsomal system induced reversed mutations in E coli strain K12, Geim et al, 1975 (186). Trichloroethylene

has also been shown to induce frameshift as well as base substitution mutation in S. cerevisiae strain XV185-14C in the presence of mouse liver homogenate, Shahin et al, 1977 (187).

#### 13.10.3.13 TERATOGENICITY

No reports indicating a teratogenic effect of trichloroethylene were found. The study of Schwetz reffered to earlier was negative at an exposure level of 300 parts per million trichloroethylene 7 hours a day on day 6 through 15 of gestation.

### 13.10.3.14 FACTORS AFFECTING TOXICITY

The cardiac arrhythmias caused by trichloroethylene under circumstances in which there are high circulating levels of epinephrine can be blocked byadministering beta adrenergic antagonists, Evreux et al, 1967 (188).

Ethyl alcohol potentiates the toxicity of trichloroethylene, Cornish et al, 1968 (189).

The effect of phenobarbital in potentiating the toxicity of trichloroethylene is unclear. In one study the administration of phenobarbital and 3-methylcholanthrene increased the hepatotoxicity of trichloroethylene as determined by measurements of serum enzymes and hepatic glucose-6-phosphatase and histological observation of liver sections. The potentiating effect was greater with phenobarbital than with 3-methylcholanthrene. The level of trichloroethylene used in these experiments was 10,400 parts per million for 4 hours, Carlson, 1974 (190).

Similar results were found in rats pre-treated with 5 different inducers of hepatic mixed-function oxidase systems including phenobarbital and 3-methylcholanthrene. When trichloroethylene anaesthesia (1 % for 2 hours) was carried out in the pre-treated animals, acute hepatic injury resulted as shown by elevation of serum transaminases, prolongation of anaesthesia recovery time, and enhanced urinary excretion of trichloroethylene metabolites, Moslen et al, 1977 (191). These results are in apparent conflict with an earlier study in which rats were pre-treated with phenobarbital and then injected with trichloroethylene in peanut oil. No potentiation of the effect of phenobarbital on the toxicity of trichloroethylene could be demonstrated, Cornish et al, 1973 (64).

### 13.10.4 HUMAN EXPERIENCE

# 13.10.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

As with many other industrial chemicals early reports of poisoning by trichloroethylene are often difficult to interpret because of the impurity of the solvent. In particular in the years prior to 1967 the manufacturing process for trichloroethylene produced an intermediate chemical 1,1,2,2-tetrachloroethane, a compound having a much higher toxicity than that of trichloroethylene. There are many case reports of trichloroethylene poisoning in the literature and as might be expected, acute exposure results predominantly in a narcotic effect with chemical burns on the skin if there is prolonged contact between the skin and liquid solvent. In a number of instances sudden death has occurred either at work or within a few hours after leaving the exposure.

These cases of sudden death are thought to be due to ventricular fibrillation.

In persons drinking trichloroethylene, liver and renal damage may be prominent effects.

In persons more chronically exposed, dizziness, headache, fatigue, nausea, vomiting, fainting spells, irritation of the eyes, and in some persons intolerance to alcohol are all complaints that may be recorded. In general, symptoms due to trichloroethylene disappear rapidly when the subject is removed from the exposure.

In a study of 104 persons exposed to trichloroethylene in a variety of industries about two-thirds of the workers examined had signs or symptoms suggestive of central nervous system depression. In those workers who left the exposure, symptoms were reported to subside within four to five months of leaving. The investigator concluded that 200 to 400 parts per million of trichloroethylene constituted too high a standard for an 8 hour daily exposure, Anderson, 1957 (192). This study, in common with many epidemiological studies, suffers from lack of precise exposure data and the subjective nature of the findings makes it difficult to isolate the effects due solely to the solvent vapors.

In a study of 50 workers in a machine factory who were continuously exposed to varying concentrations of trichloroethylene it was possible to divide the workers into three groups depending upon the level of exposure to trichloroethylene. It was believed that Group A was exposed to between 150 and 250 parts per million while Group B was exposed to



50 to 100 parts per million and Group C had exposures averaging below 50 parts per million. Group A had more central nervous system effects including dizziness, a feeling of drunkenness, headaches, and flushing of the face, and irritation of the throat. Group B reported headaches, irritation of the eyes, flushing of the face and fatigue, but no sensation of drunkenness or giddiness. Group C reported no symptoms, Takamatsu, 1962 (193).

In a study of 122 workers,50 % of the workers complained of symptoms such as headache, irritability, abnormal fatigue, and intolerance of alcohol. The investigators related these symptoms to the level of trichloracetic acid in the urine and found that 50 % of the workers with subjective disorders were found in workers who excreted 40 to 70 mg of trichloroethanol per litre of urine. In persons who excreted less than 20 mg per litre of trichloroethanol there were no subjective complaints, Ahlmakr et al, 1951 (194).

Intentional or accidental ingestion of trichloroethylene may result in coma and death, liver and kidney toxicity and cardiac arrhythmias.

The dosage that will produce coma in adult humans is thought to lie between 50 and 150 ml, Aviado et al, 1976 (181).

As with many good fat solvents, frequent contact with the skin produces dryness and cracking and may result in generalized dermatitis or skin infections.

#### 13.10.4.2 HEMATOPOIETIC SYSTEM

No reports of significant effects of trichloroethylene on the hematopoietic system of humans have been found.

### 13.10.4.3 NERVOUS SYSTEM

Trichloroethylene has been used for many years as an anaesthetic and analgesic but its use has declined with the advent of more effective anaesthetic agents.

One feature which appeared to be unique to trichloroethylene was the production of a specific paralysis of the trigeminal nerve (195). Later this effect was thought to be due to the production of dichloroacetylene through passage of the trichloroethylene through the soda lime cannisters of anaesthetic machines. The reaction of trichloroethylene with the alkali produces dichloroacetylene. No reports of trigeminal nerve paralysis have been found in persons exposed in industry.

### 13.10.4.4 RENAL SYSTEM

Although acute renal failure due to trichloroethylene has been reported, Gutch et al, 1965 (196), this is a rare event and trichloroethylene is much less toxic to the kidney than carbon tetrachloride.

### 13.10.4.5 GASTROINTESTINAL TRACT

Apart from the nausea accompanying high levels of exposure to trichloroethylene no other effects of exposure to this solvent on the gastrointestinal tract have been reported.

### 13.10.4.6 LIVER

Human experience of exposure to trichloroethylene shows that this solvent has a low toxicity for the liver. In 27 of 35 patients given trichloroethylene as an anaesthetic, the cephalin cholesterol flocculation

test was positive immediately after the anaesthesia but the test was negative two weeks later, Armstrong, 1947 (197).

In 12 workers in a degreasing shop who had been exposed to trichloroethylene for a minimum of 5 years, there was no evidence of liver injury as revealed by a comprehensive series of liver function tests although the exposure was above the level of 3 mg of trichloroethylene per litre of air, Tolot et al, 1964 (198).

In 18 workers none of whom were alcoholics but were exposed to trichloroethylene, there were some abnormalities of cephalin flocculation, total lipids and unsaturated fatty acids, together with an increase in beta and gamma globulins, Guyotjeannin et al, 1958 (199).

### 13.10.4.7 CARDIOVASCULAR SYSTEM

In 200,000 women given trichloroethylene as an analgesic during therapeutic abortions. 7 women died from cardiac arrest and these deaths might be related to the trichloroethylene exposure, Radinov et al, 1973 (200). In industrial exposure, a number of sudden deaths attributed to ventricular fibrillation have been reported in persons exposed to high levels of trichloroethylene, Kleinfeld et al, 1954 (201), James, 1963 (202), Bell, 1951 (203). The development of an animal model Reinhardt et al, 1973 (135), supports the theory that sudden deaths connected with exposure to certain chlorinated hydrocarbon solvents are due to sensitization to circulating epinephrine.

# 13.10.4.8 RESPIRATORY SYSTEM

No reports of specific effects of trichloroethylene on the human respiratory system have been found.

## 13.10.4.9 REPRODUCTIVE SYSTEM

No reports of the effect of trichloroethylene on the human reproductive system have been found.

# 13.10.4.10 ENDOCRINE SYSTEM

No reports of the effects of trichloroethylene on the human endocrine system have been found.

# 13.10.4.11 EYES AND OTHER SENSE ORGANS

Trichloroethylene vapor is irritating to the eyes and mucous membranes producing a burning or dry sensation in the throat and a burning sensation in the eyes. As previously noted the odor threshold for trichloroethylene is about 21 parts per million.

#### 13.10.4.12 CARCINOGENICITY

No reports suggesting that trichloroethylene is carcinogenic in man have been found.

#### 13.10.4.13 MUTAGENICITY

No reports suggestive of the mutagenicity of trichloroethylene in man have been found.

### 13.10.4.14 TERATOGENICITY

No reports of the teratogenicity of trichloroethylene in man have been found.

# 13.10.4.15 FACTORS AFFECTING HUMAN RESPONSE

There have been reports that persons exposed to trichloroethylene at work and who then drink an alcoholic beverage may experience intense flushing of the face - the so-called "degreasers flush". The mechanism for this effect is unclear although it appears to be a potentiation of trichloroethylene toxicity by alcohol, but the effect is not due purely to a high blood trichloroethylene concentration since it is possible to elicit the skin response days following the last exposure to trichloroethylene at a time when only trace amounts of the solvent would be circulating.

It has been suggested that a threshold amount of one of the metabolites of trichloroethylene must be present before alcohol can cause the dermal response. It is known that the major metabolites of trichloroethylene are cumulative and are detectable for weeks following cessation of long-term vapor exposure.

It is reported that the dermal response can occur as long as six weeks following a five day exposure to trichloroethylene at a level of 200 parts per million, Stewart et al, 1974 (204).

# 13.11 TETRACHLOROETHYLENE

### 13.11.1 SUMMARY OF BIOLOGICAL INFORMATION

Central nervous system depressant. No chronic effects in man, rats, monkeys and guinea pigs have been reported below 400 ppm.

Mild reversible, central nervous system depression is reported at levels down to 100 ppm. Present occupational limit is 50 ppm TWA with "Ceiling" value at 100.

Note that Trichloroethylene is very similar to Tetrachloroethylene in toxicity; difference in rating based solely on evidence of cancer in rats at high levels of TCE.

Low

Toxicity Rating: [C]

### Toxicity to Animals

Test Rating
Acute Low

#### Toxicity to Man

Test Rating

Experimental Low

Epidemiological Low

#### 13.11.2 METABOLISM

Chronic

Because of its high fat solubility tetrachloroethylene accumulates in fatty tissue which leads to a very long biological half-life in the body. Almost all of the tetrachloroethylene absorbed is eliminated through the lungs and relatively little is metabolized in humans. The

long biological half-life, however, means that periods as long as two weeks may be required to completely eliminate the tetrachloroethylene retained during a single 8 hour exposure to 100 parts per million, Fernandez et al, 1976 (205). The metabolism of tetrachloroethylene proceeds through an epoxide intermediate to trichloroacetic acid and a small amount of trichloroethanol and other as yet unidentified trichloro compounds which are found in the urine of exposed humans and also in rats and mice. The biological half-life of retained tetrachloroethylene in humans after exposure to 10 to 100 parts per million of tetrachloroethylene 8 hours a day 5 days a week was approximately 144 hours, Ikeda et al, 1973 (165). After exposure to tetrachloroethylene the net excretion of trichloroacetic acid in the urine increased daily and reached a maximum 3 to 4 days after exposure, Tada et al, 1969 (206).

#### 13.11.2.1 ABSORPTION

Tetrachloroethylene is rapidly and mainly absorbed through the lungs and is also readily absorbed from the gastrointestinal tract, but very little is absorbed through the skin, Stewart et al, 1964 (20).

#### 13.11.2.2 DISTRIBUTION AND RETENTION

Few actual determinations of tissue levels of tetrachloroethylene have been made during life, but a mathematical model has been derived based on results from 25 human subjects exposed to 50 to 150 parts per million of tetrachloroethylene for up to 8 hours. The excretion of tetrachloroethylene was measured in the expired air and to allow for

the construction of a mathematical model the tissues of the body were classified into four groups, those which were rich in blood vessels (brain, heart, liver, kidney and endocrine glands); the muscle group (muscle and skin); the fat group (adipose tissue and bone marrow); and finally the tissues poor in blood vessels (bone cartilage and ligaments). It was predicted from the mathematical model that after exposure rapid depletion of the tissues rich in blood vessels would take place followed more slowly by the muscle group and the tissues poor in blood vessels and finally the fat group would begin to give up its tetrachloroethylene starting about 8 hours after the end of exposure, Guberan et al, 1974 (207).

### 13.11.2.3 ELIMINATION

As mentioned in the preceding sections tetrachloroethylene is excreted in the breath for long periods after exposure. Exposure of five female mice to 14C-tetrachloroethylene vapor (1.3 mg/gram body weight) for 2 hours resulted in 90 % absorption of the solvent, of which 70 % was subsequently expired in the air, 20 % was excreted in the urine, and 0.5 % was excreted in the feces during 4 days of measurement, Yllner, 1961 (208). Fractionation of urinary metabolites resulted in the identification of trichloracetic acid (52 %) oxalic acid (11 %), dichloroacetic acid (trace), and other unidentified, polar labelled compounds (18 %). Monochloroacetic acid, formic acid, and trichloroethanol were not identified as metabolites. When humans were exposed by inhalation to tetrachloroethylene (87 parts per million)

for 3 hours, trichloroacetic acid and unidentified trichloro-compounds were found in the urine. The concentration of trichloroacetic acid in the urine increased during exposure and had returned to nearly normal 64 hours after exposure. The total trichloro compounds recovered in the urine were equivalent to only 2.8 % of the retained tetrachloro-ethylene, 1.8 % of this being trichloroacetic acid. Only 4 % of the retained dose was metabolized, Ogata et al. 1971 (209).

# 13.11.3 ANIMAL EXPERIMENTAL STUDIES

## 13.11.3.1 HEMATOPOIETIC SYSTEM

No reports of effects of tetrachloroethylene on the hematopoietic system were found.

## 13.11.3.2 NERVOUS SYSTEM

In common with a number of other halogenated hydrocarbons tetrachloroethylene is a central nervous system depressant. Effects of the central
nervous system of rats were apparent after 0.2 hours at 3000 parts per
million but several hours were necessary to induce unconsciousness. No
deaths were observed at 4 hours in this experiment but 20 % of the
animals died within 8 hours. Unconsciousness resulted after several
minutes at 6000 parts per million. No deaths were observed at 0.6
hours but 8 hours at this concentration proved fatal to 85 % of the
animals, Rowe et al, 1952 (210). In experiments of longer duration
rats exposed to average of 70, 230, and 470 parts per million of
tetrachloroethylene for 8 hours a day 5 days a week over a period of
7 months gave the following results: at 70 parts per million no toxic

effects were observed; however, at 230 parts per million, some animals showed congestion of the kidneys and light granular swelling but no sign of progressive injury to the liver. At 470 parts per million, the liver was congested, and cloudy swelling was apparent. Increased secretion, cloudy swelling and desquamation were observed in the kidneys, and congested was noted in the spleen as well, Carpenter, 1937 (211). In a study extending over 12 months two groups of rats, consisting of 192 animals each (96 male and 96 female) were exposed respectively to 300 and 600 parts per million of tetrachloroethylene vapor for 6 hours per day, 5 days per week, for 12 months. No signs of central nervous system depression were observed during these exposures, Leong et al, 1975 (212).

## 13.11.3.3 RENAL SYSTEM

In 12 rabbits exposed to tetrachloroethylene at a level of 2,280 parts per million for 45 days, renal function was disturbed with renal tubular function more affected than the glomerular capacity as measured by creatinine clearance and para-amino-hippuric acid, Broncaccio et al, 1971 (213).

In an early report of exposure of rats at a level of 130 parts per million for 150 exposures, kidney congestion was found while at 230 parts per million some kidney changes were found after 21 exposures and, in most rats, no liver pathology was found at this level of exposure, Carpenter, 1937 (211).



## 13.11.3.4 GASTROINTESTINAL TRACT

No reports of the effects of tetrachloroethylene on the gastrointestinal tract were found.

#### 13.11.3.5 LIVER

Guinea pigs appear to be particularly sensitive to the hepatotoxic effects of tetrachloroethylene. After 169 seven hour exposures to 400 parts per million of tetrachloroethylene, guinea pigs exhibited fatty degeneration of the liver with slight cirrhosis. Rats, rabbits, and monkeys were not affected by similar treatment, Rowe et al, 1952 (210).

In a study in which the potency ratios (LD50/ED50) for six halogenated hydrocarbons were compared, it was found that whereas carbon tetrachloride had a potency ratio which was quite large and quite different from those established for the other halogenated hydrocarbons, the potency ratio for tetrachloroethylene was 1.0. This indicates that the dose which produces liver injury is essentially identical to the dose that produces death by central nervous system depression. In contrast the potency ratio for carbon tetrachloride was 280, meaning that the effective dose for producing liver injury in mice was about 1/300th of the dose required to produce death, primarily by central nervous system depression. When severity of liver injury induced by minimal lethal doses of halogenated hydrocarbons were placed in rank order, carbon tetrachloride came first and tetrachloroethylene was fifth in order, Plaa, 1976 (74).

### 13.11.3.6 CARDIOVASCULAR SYSTEM

Unlike a number of other chlorinated hydrocarbons tetrachloroethylene does not sensitize the dog's heart to circulating epinephrine at either the 0.5 % or 1 % concentration. This is in contrast to the effects seen with trichloroethylene when at the 0.5 % level 1 out of 12 dogs showed marked cardiac arrhythmias and at the 1 % level 7 out of the 12 dogs showed such marked arrhythmias and there was one death at this concentration. The fact that tetrachloroethylene did not produce sensitization at 0.5 % or 1 % does not mean that at higher levels abnormalities of cardiac rhythm may not be caused.

#### 13.11.3.7 RESPIRATORY SYSTEM

No reports of adverse effects of tetrachloroethylene on the respiratory system were found.

#### 13.11.3.8 REPRODUCTIVE SYSTEM

In a study of mice and rats exposed at 300 parts per million of tetrachloroethylene for 7 hours a day on day 6 through 15 of gestation there was a relative increase in maternal liver weights of mice, a decrease in maternal body weights of rats, and an increase in incidence of fetal resorption in rats. In fetal mice, there were decreased body weights and increased incidence of subcutaneous edema, delayed ossification of skull bones, and split sternebrae, Schwetz et al, 1975 (24).

Exposure of female rats to 300 mg per cubic metre (44 parts per million) for the entire gestation period caused a decrease in the level of DNA and total nucleic acids in the liver, brain, ovaries and placenta, Ananina, 1972 (214).



### 13.11.3.9 ENDOCRINE SYSTEM

The effects of tetrachloroethylene on the adrenal gland were measured in rabbits inhaling 2,790 parts per million tetrachloroethylene 4 hours per day, 5 days per week, for 9 weeks. Urine and plasma levels of adrenocortical and adrenomedullary hormones were measured, as well as excretion of the hormone metabolite. Although no statistically significant differences were found, both cortical and medullary hormones were increased with tetrachloroethylene exposure, Mazza et al, 1971 (215).

### 13.11.3.10 EYES AND OTHER SENSE ORGANS

Tetrachloroethylene is moderately irritating to the eyes, mucous membranes and upper respiratory tract.

#### 13.11.3.11 CARCINOGENICITY

The draft report of the U.S. National Cancer Institute, Carcinogenesis Bio-Assay Report on Tetrachloroethylene was released in March, 1977.

The statistical analysis of the data indicates that tetrachloroethylene is not carcinogenic in the test rat strain but was carcinogenic in the test mouse strain. The average oral dose levels of tetrachloroethylene used in the studies were as follows: male rats 517 and 1,034 mg per kg of body weight, male mice 536 and 1,072 mg per kg of body weight; female rats 521 and 1,042 mg per kg of body weight; female mice 368 and 772 mg per kg of body weight. In male mice, hepatocellular carcinoma of the liver was found in large numbers in the dosed groups. These results were highly significant whether using the untreated matched controls or the matched vehicle controls.

Similar results, only less significant, are found for female mice with regard to hepatocellular carcinoma of the liver. These studies were conducted with the maximum tolerated dose and approximately one half of the maximum tolerated dose. It should be noted that this methodology is now being studied by the National Cancer Institute and some modification of future test protocols is possible.

#### 13.11.3.12 FACTORS AFFECTING TOXICITY

In experiments in which liver microsomal enzymes were induced in rats by phenobarbital injections prior to exposure to tetrachloroethylene vapor the toxicity of the tetrachloroetylene was not enhanced by the enzyme induction. In contrast to these results the toxicity of carbon tetrachloride and chloroform were both increased, Cornish et al, 1973 (64).

In studies in which tetrachloroethylene was mixed with benzene and with toluene for LD-50 studies in rats, mixtures containing tetrachloroethylene and benzene gave LD-50 values which were slightly less than additive while mixtures containing both tetrachloroethylene and toluene had inconsistent LD-50 values, Withey et al, 1975 (216).

#### 13.11.4 HUMAN EXPERIENCE

#### 13.11.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

In 13 volunteers having an average age of 34.5 years who were exposed to 87 parts per million of tetrachloroethylene for 3 hours and in whom the water soluble metabolites were measured at intervals during

and after exposure, excretion of trichloroacetic acid increased progressively from the start of the exposure until 3 hours following exposure. Only about 1.8 % of the abosrbed tetrachloroethylene was excreted as trichloroacetic acid and the excretion of this compound reached the normal level 64 hours after exposure. It was concluded from these studies that although some tetrachloroethylene was excreted through the lungs the major part of the solvent was retained in the body during the first 67 hours after exposure, Ogata et al, 1971 (217). These experimental results were found in male volunteers who were exposed to 390 mg/litre tetrachloroethylene for 6 hours with two 30 minute breaks. 25 % of the absorbed tetrachloroethylene was excreted by the lungs, 10 % of the absorbed solvent was excreted as metabolites in the urine and 62 % was retained in the body, Bolanowska et al, 1972 (218).

In studies in human volunteers the first complaints were of mild eye irritation and congestion of the frontal sinuses at levels between 83 and 130 parts per million. At levels between 200 and 235 parts per million the odor was immediately apparent but acclimation readily occurred with eye irritation developing in 20 to 30 minutes and persisting. Slight dizziness and sleepiness was noted by some individuals. At levels between 200 and 350 parts per million there was a burning sensation in the eyes, congestion of the frontal sinuses, lightheadedness, transient nausea in some individuals, and impaired motor coordination requiring extra mental effort to carry out movements. Recovery occurred within one hour of

leaving the exposure. At levels between 500 and 690 parts per million the exposure was felt to be unpleasant. There was marked eye and nasal irritation, dizziness, tightness and numbness of the mouth, loss of inhibitions, motor coordination was only possible with considerable mental effort. Recovery again occurred within one hour of leaving the exposure. At levels between 930 and 1185 parts per million there was marked irritation of the eyes and upper respiratory tract after 2 minutes of exposure, and dizziness became pronounced. Recovery was rapid on leaving the chamber, Rowe et al, 1952 (210).

In a study of 113 workers in 46 dry cleaning plants in Germany 35 % of the workers complained of headaches, 34 % of insomnia, 29 % of dizziness, and 20 % of "heart" complaints. Medical examination of the workers revealed hyperhidrosis, dermagraphism, and tremors in 40 % of the workers and mucous membrane irritation in 33 %. 326 measurements of air concentrations of tetrachloroethylene were made in the 46 plants and of these measurements 75 % were less than 100 parts per million. In one plant measurements taken at various locations every 15 minutes during a 2 hour drying process showed that air concentrations of tetrachloroethylene never exceeded 80 parts per million. During spot removal operations in another plant tetrachloroethylene concentrations ranging from 100 to 280 parts per million were found (195). Laboratory studies of the workers and 43 control subjects showed that only thymol turbidity and bilirubin determinations were significantly affected by the tetrachloroethylene exposure. No reports of other epidemiological studies in which the data permitted dose response relationships to be studied have been found.



## 13.11.4.2 HEMATOPOIETIC SYSTEM

No reports of effects of tetrachloroethylene on the human hematopoietic system have been found.

#### 13.11.4.3 NERVOUS SYSTEM

As has been previously pointed out, even an acute exposure to tetrachloroethylene may in fact represent a chronic exposure due to retention of the compound in the body for long periods after the exposure has ended. As with many industrial chemicals, there are numerous reports of CNS effects but seldom is the exposure data available or if available of sufficient quality to enable correlations between the level of exposure and the effect to be determined. A review of personal communications and translations of Soviet literature was made on the peripheral neuropathies produced by tetrachloroethylene. Fifteen cases of diagnosed peripheral neuritis correlated with exposure to tetrachloroethylene or unspecified chlorinated hydrocarbons were cited from U.S.A. reports and 145 cases of various peripheral neuropathies from unspecified chlorinated hydrocarbons were cited in the Soviet literature (195).

In a very few cases local effects through splashing of tetrachloroethylene on the skin have been reported with numbness and weakness or paralysis of the underlying muscle, Eberhardt et al, 1966 (219).

In a study of 20 workers in 5 dry cleaning plants neurological testing and medical examinations were carried out and several behavioral tests administered at the beginning of each work day. Breath samples

were collected at the time of the test and every 2 hours during the day. The time weighted average concentrations of tetrachloroethylene were also calculated and ranged from 1.32 parts per million for five counter workers to 37.2 parts per million for five machine operators. While the results of the behavioral tests showed no significant difference in the performance of the two groups, correlations were shown between years of exposure and the digit symbol test, the neisser letter research test, the critical flicker fusion frequency, and three Santa Anna finger dexterity scores. It may be significant in interpreting the results of these tests that the unexposed workers had a mean age of 34.44 years while the exposed workers had a mean age of 43.45 years (195).

## 13.11.4.4 RENAL SYSTEM

Although there have been a very few reports of renal damage attributed to tetrachloroethylene, in no case has the exposure been only to tetrachloroethylene and in each case there is evidence that the exposure to tetrachloroethylene was very high, both due to inhalation of the vapor and to skin contact with the liquid solvent. In one case there was a history of alcoholism with hepatomegaly being diagnosed two years prior to the occupation exposure to tetrachloroethylene, Dumortier et al, 1964 (220).

#### 13.11.4.5 GASTROINTESTINAL TRACT

No reports of effects of tetrachloroethylene on the gastrointestinal tract in humans have been found.

### 13.11.4.6 LIVER

Reports of controlled exposures to tetrachloroethylene including liver function tests have not been found, but liver damage as a result of accidental exposure has been reported on a number of occasions.

One case of cirrhosis of the liver and three cases of probable liver damage were reported in nine workers who had used a solvent containing 99 % tetrachloroethylene for over a year. The liver damage was measured by increased BSP dye retention, elevated urinary urobilinogen and a positive cephalin flocculation test. None of these workers were reported to have high alcohol consumption, Coler et al, 1953 (221).

Liver toxicity diagnosed by abnormal alkaline phosphatase, SGOT, bilirubin and cephalin flocculation measurements, were reported in two women who had worked for 2-1/2 months, 10 hours a day, exposed to tetrachloroethylene. Liver biopsy two weeks after the end of the exposure showed degeneration of parenchymal cells, focal collections of mononuclear cells, and exaggeration of liver sinusoids. The liver was still enlarged six months after this examination, Mecklar et al, 1966 (222).

Only slight liver damage was reported in a man exposed for six years to unknown levels of tetrachloroethylene. The liver damage was diagnosed on the basis of an elevated serum bilirubin and prolonged BSP retention time. The test results were reported to have returned to normal 20 days after removal from the exposure, Von Oettingen, 1964 (223). In a workman exposed to one gallon of tetrachloroethylene

and 50 % Stoddard solvent for 3-1/2 hours, unconsciousness was produced and elevation of urinary urobilinogen and serum bilirubin occurred 9 days after the exposure. The alkaline phosphatase measurements became elevated two weeks after exposure and SGPT was elevated on the eighteenth day after exposure. Simulation of the exposure conditions resulted in an estimate of the concentration of tetrachloroethylene during the exposure to range from 25 to 1,470 parts per million, Stewart et al., 1961 (224).

## 13.11.4.7 CARDIOVASCULAR SYSTEM

No reports of effect of tetrachloroethylene on the cardiovascular system of humans have been found.

### 13.11.4.8 RESPIRATORY SYSTEM

No reports of adverse effects of tetrachloroethylene on the respiratory system have been found.

### 13.11.4.9 REPRODUCTIVE SYSTEM

No reports of effects of tetrachloroethylene on the human reproductive system have been found.

#### 13.11.4.10 ENDOCRINE SYSTEM

No reports of effects of tetrachloroethylene on the human endocrine system have been found.

#### 13.11.4.11 EYES AND OTHER SENSE ORGANS

The odor threshold for tetrachloroethylene is reported to be 4.6 parts per million and at higher concentrations the vapor is irritating

to the eyes, nose and throat.

## 13.11.4.12 CARCINOGENICITY

No reports of a carcinogenic effect of tetrachloroethylene in humans were found.

### 13.11.4.13 MUTAGENICITY

No reports of mutagenicity due to tetrachloroethylene in humans were found.

### 13.11.4.14 TERATOGENICITY

No reports suggestive of teratogenic effect of tetrachloroethylene in humans were found.

# 13.11.4.15 FACTORS AFFECTING HUMAN RESPONSE

In common with other solvents having a pungent smell, asthmatic attacks have been reported to be induced in known asthmatics exposed to high concentrations of tetrachloroethylene vapor, Palecek, 1970 (225).

### 13.12 CHLOROPRENE

## 13.12.1 SUMMARY OF BIOLOGICAL INFORMATION

Chloroprene causes central nervous system depression with damage to lungs, liver, and kidneys in rats. Chloroprene has an effect on the developing fetus. Russian epidemiological studies have shown a dose related increase in the incidence of lung and skin cancer in chloroprene workers, changes in spermatogenesis, chromosomes and an increase in abortions were also reported in the two Russian references. The concentrations of chloroprene associated with these changes were from 1 to 7 mg/m<sup>3</sup> (3.5 - 24 ppm). If these results are confirmed a downward revision of the present 25 ppm TWA occupational limit can be expected. Carcinogen in man.

Toxicity Rating: [A]

## Toxicity to Animals

Test	Rating
Acute	High
Chronic	High

#### Toxicity to Man

<u>Test</u>	Rating
Experimental	
Enidemiological	High

### 13.12.2 ANIMAL EXPERIMENTAL STUDIES

Exposure to chloroprene vapor causes irritation of the respiratory tract and central nervous system depression. Even at low concentrations (1.7 mg/cu. metre) 4-1/2 months of exposure in male rats caused a

reduction in the number of normal spermatogonia, an increase in the number of dead spermatogonia and a decrease in the motility of spermatazoa. A study in mice at a concentration of 1.7 mg/cu metre caused increase in the number of testicular tubules with desquamating germinal epithelium. A level of 0.064 mg/cu metre had no adverse effect on the mouse gonads. Exposure to a concentration of 4 mg/cu metre at various times during pregnancy led to teratogenic effects. Cerebral hernia occurred in fetuses when exposures took place on days 5 to 6, 9 to 10, 11 to 12, or 13 to 14 of pregnancy. In the offspring whose mother had been exposed to 4 mg/cu metre of chloroprene during the entire pregnancy a decrease in the rate of weight gain was found and a concentration of 0.6 mg/cu metre chloroprene increased numbers of deaths in the first three weeks after birth and a reduction in the rate of weight gain were noted. Even at a dosage of 0.13 mg/cu metre an increase was noted in postnatal deaths of the offspring of the exposed mothers. Chloroprene failed to produce any abnormalities in the offspring when the mothers were exposed at a concentration of 0.056 mg/cu metre, Sanotskii, 1976 (226).

#### 13.12.3 HUMAN EXPERIENCE

As in the animal studies, the primary response to chloroprene is of central nervous system depression and there may also be injury to lungs, liver and kidneys as well as effects due to irritation leading to dermatitis, conjunctivitis, corneal necrosis and temporary loss of hair. Examination of Russian chloroprene workers has been reported to show

functional disturbances in spermatogenesis after 6 to 10 years of work in chloroprene production. A questionnaire is said to have revealed three times the frequency of spontaneous abortion in wives of chloroprene workers compared with the control group. The frequency of cells with chromosome aberrations was also reported to be considerably higher in the chloroprene exposed group than in the control group, Sanotskii, 1976 (226). Two Russian reports have suggested that chloroprene exposure is associated with an increased incidence of skin and lung cancer. These studies were the result of a large scale epidemiological investigation of chloroprene workers in the Yerevan region of Russia. The incidence of skin cancer was greatest in the chloroprene exposed group and was substantially greater than for the three unexposed groups. A gradient in skin cancer incidence was seen among five groups reflecting increasing levels of chloroprene exposure.

The group of chloroprene workers also experienced the highest incidence of lung cancer and again a gradient in lung cancer incidence was demonstrated according to the exposure group, Lloyd et al, 1975 (227). Chloroprene causes Salmonella typhimurium TA100 strain in the absence of any metabolic activation system to show a linearly increasing mutagenic response with increasing concentrations of chloroprene ranging from 0.5 to 8 % in air, Bartsch et al, 1975 (162).



#### 13.13 MONOCHLOROBENZENE

Because of the relative paucity of data relating to the health effects of monochlorobenzene a summary format will be adopted in this report rather than the extended form used elsewhere.

### 13.13.1 SUMMARY OF BIOLOGICAL INFORMATION

Irritant to eyes, skin and upper respiratory tract. Central nervous system depressant. Causes damage to liver, lungs and kidney.

Occupational exposure limit 75 ppm (TWA). No evidence of carcinogenicity but has not undergone adequate testing.

Toxicity Rating: (

Toxicity to Animals

Test Rating

Acute Low

Chronic Moderate

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological Moderate

## 13.13.2 ANIMAL STUDIES

Little information is available on the absorption of monochlorobenzene, but being one of the more volatile halogenated benzenes readily exreted from the lungs, it is to be expected that the compound would be readily abosrbed from the lungs. Although no information was found upon the absorption of monochlorobenzene through the skin or from the gut it

would be expected that the compound would be absorbed by these routes and skin absorption should be considered a potential hazard until further data becomes available.

Approximately 27% of an oral does of 0.5 mg/Kg of body weight monochlorobenzene was excreted through the lungs of rabbits. 25% of the dose was excreted conjugated with glucuronic acid and 27% as ethereal sulfates. Azouz et al, 1952 (228).

Monochlorobenzene is also excreted conjugated with glutathione (mercapturic acids) and in rabbits. This accounts for about 25% of the dose.

Monochlorobenzene, being liquid soluble, is distributed throughout mammalian tissues and appears to traverse most tissue barriers including the brain and the placenta. The hepatic necrosis produced by exposure to monochlorobenzene results from its conversion to reactive toxic intermediates in the liver. The stimulation of microsomal enzyme systems by pretreatment with phenobarbital potentiates the hepatic damage of monochlorobenzene, Brodie et al, 1971 (229), Mitchell et al, 1971 (230). There is evidence that some of the oxidations proceed through the formation of arene oxide intermediates. This evidence includes: a correlation of metabolism with overall toxicity and cellular toxicity; a correlation of toxicity with in vivo and in vitro covalent binding of metabolites with cell proteins; and the appearance of increased toxicity associated with depletion of tissue levels of glutathione, Reid et al, 1973 (231).

It has been shown in rats that administration of 500 to 800 mg/Kg of body weight of chlorinated benzenes leads to hepatic porphyria characterized by elevated levels of precursor porphyrins in liver and feces. The first signs of intoxication are an increase in urinary coproporphyria and porphobilinogen. Aminolevulinic acid excretion was a late effect, Rimington et al, 1963 (232). Porphyria is a disturbance in porphyrin metabolism and is characterized by increased formation of and excretion of prophyrin precursors, cutaneous photosensitivity, frequent episodes of hemolytic anemia and splenomegaly. Acute abdominal and nervous system manifestations may also occur.

Monochlorobenzene produces sedation, analgesia and anaesthesia after oral or parenteral administration. Relatively large doses of monohalogenated benzenes are necessary to produce acute poisoning although chronic effects may occur at relatively low doses. Acute poisoning is characterized by symptoms primarily originating in the nervous system. There may be hyperexcitability, restlessness, muscle spasms or tremors, followed by varying degrees of central nervous system depression.

Halogenated benzenes like aliphatic halogenated hydrocarbons are thought to sensitize the myocardium to circulating epinephrine and this may result in ventricular arrhythmias and sudden death, Von Oettingen, 1955 (233).

Subcutageous injection of 4 to 5 grams per kilogram of body weight of monochlorobenzene caused no immediate effect but resulted in death

within a few days. On autopsy the rats were found to have necrosis of the liver and kidneys. 7 to 8 grams per kilogram of body weight of monochlorobenzene given subcutaneously was fatal within a few hours to rats, Von Oettingen, 1955 (233).

The halogenated benzenes are stored in fat and chronic effects of exposure to monochlorobenzene apart from the risk of porphyria mentioned earlier include blood dyscrasias and death, if it occurs, may be due to toxic depression of the bone marrow, the pancytopenia leading to hemorrhage and overwhelming infection, Robinson et al, 1975 (234).

Halogenated benzenes are irritating to eyes and mucosa.

No studies of the effects of monochlorobenzene on reproduction, teratogenicity or mutagenicity have been found. No reports of carcinogenic tests lasting over a year in duration have been found and because the halogenated benzenes form arene oxide intermediate compounds which have been associated with mutagenesis and carcinogenesis, it must be concluded that no satisfactory testing of the carcinogenicity of monochlorobenzene has been carried out.

## 13.13.3 HUMAN EXPERIENCE

Human exposure to monochlorobenzene causes headaches, irritation of the eyes and upper respiratory tract, numbness, inhibition and eventual loss of consciousness. In contrast to benzene and hezachlorocyclohezane, the skin irritation due to contact with monochlorobenzene appears to last for a long time and may progress to hyperemia and wheal formation, Von Oettingen, 1955 (233).

No reports of chronic illness due to monochlorobenzene have been found.

13.14 DICHLOROBENZENE

13.14.1 SUMMARY OF BIOLOGICAL INFORMATION

Ortho Dichlorobenzene is more toxic than para dichlorobenzene.

Both are irritant to eyes and nose and produce liver damage and depression of white cell count in animals. Metabolism to arene oxide raises possibility of carcinogensis but no adequate animal testing has been done to prove whether dichlorobenzene is carcinogenic in animals.

No evidence for carcinogenesis in man. High exposure in man (moth repellents, deodorizers) has resulted in nausea, weakness and jaundice.

Very little dose - response information available. Because of metabolism and reports of effects on blood these compounds should be treated with suspicion as possibly proving to be more toxic than presently considered. Occupational limit, o-dichlorobenzene 50 ppm, p-dichlorobenzene 75 ppm.

Toxicity Rating: [B]

Toxicity to Animals

<u>Test</u> <u>Rating</u>

Acute Moderate

Chronic Moderate

Toxicity to Man

Test Rating

Experimental No Data

Epidemiological Moderate

### 13.14.2 ANIMAL EXPERIMENTAL STUDIES

Dichlorobenzene, being lipid soluble, is distributed throughout mammalian tissues and appears to traverse most tissue barriers including the brain and placenta.

The dichlorobenzenes are absorbed through the gastrointestinal tract, the intact skin and the lungs. After oral administration (0.5 mg/kg of body weight) to rabbits the dichlorobenzenes were slowly metabolized by oxidation mainly to dichlorophenols (235). The peak excretion of the phenols and their conjugation products occurs on the first day for the ortho and meta isomers and on the second day for paradichlorobenzene (236). All of the halogenated benzenes like benzene, produce an array of central nervous system effects when given orally. The central nervous system effects are stimulation at low doses and depression at higher doses. The LD-50 for paradichlorobenzene for the rat given the material by mouth is 500 mg/kg of body weight and in the mouse 9,250 mg/kg of body weight (237). Doses of orthodichlorobenzene of 0.25 and 0.5 ml/kg of body weight given intravenously to rabbits were fatal within 24 hours and doses of 1 ml/kg of body weight given intravenously were fatal within 20 seconds. Histological examinations of animals given lethal doses of orthodichlorobenzene showed damaged liver and kidneys (238).

Paradichlorobenzene is said to be much less toxic than orthodichlorobenzene although the LD-50's for both compounds are not dissimilar except for the guinea pig which appears to be roughly twice as resistant to paradichlorobenzene than to orthodichlorobenzene (237).

Orthodichlorobenzene is absorbed through the intact skin and repeated subcutaneous injections of orthodichlorobenzene in rabbits produced blood dyscrasias characterized by granulocytosis with little or no effect on red blood cells. Inhalation of orthodichlorobenzene by rats at 800 parts per million for 11 to 20 hours was irritating to the eyes and nose and produced slight changes in the tubular epithelium of the kidney. This level of exposure finally resulted in massive necrosis of the liver (238). Rabbits exposed continuously to 100 mg/litre of paradichlorobenzene showed irritation of the eyes, nose, and showed muscular twitching, tremors, central nervous system depression, nystagmus and rapid labored breathing. The rabbits recovered within 30 to 120 minutes after exposure. Granulocytopenia occurred and persisted for three weeks after the exposure ended (239). Paradichlorobenzene produces histological changes in kidneys, liver, spleen and heart in a number of mammalian species and these changes include cloudy swelling, vacuolization and necrosis (240).

Only one study of the mutagenicity of dichlorobenzene was found in which the mitoses in rat lung cell cultures were studied. The dose of 5 micrograms did not produce any significantly different number of mitoses than in the control animals and it did not exert any inhibitory effect on the cultures. The conclusions from this study are that under the conditions of the study dichlorobenzene did not exert a mitotic effect (241). No other reports of mutagenic data for dichlorobenzene have been found. In a study conduced in 1961 dichlorobenzene gave a slight



response for carcinogenic activity in mice, as measured by the sebaceous gland and the hyperplasia tests. In both cases dichlorobenzene (1 gram/100 ml of solution in acetone) was applied to the skin of Swiss mice three times as a 0.1 ml solution (242). Another study investigated the effects of paradichlorobenzene induced resistance to a transplanted leukemia in the rat. It would appear from this study that paradichlorobenzene modified the induced resistance of the rats to the leukemia. However, there was not sufficient evidence to state that there are immunosuppressant effects resulting from exposure to paradichlorobenzene (243).

### 13.14.3 HUMAN EXPERIENCE

There have been three reports in the literature of leukemia following chronic exposure to orthodichlorobenzene. In one case a man developed chronic lymphoid leukemia after working with a solvent containing 80 % orthodichlorobenzene and 15 % paradichlorobenzene for 10 years. A girl developed acute myeloblastic leukemia and was reported to have a neurotic compulsion to remove dirt and grease stains from her clothes which she did repeatedly with a product containing 37 % orthodichlorobenzene. Another man exposed to a glue containing 2 % orthodichlorobenzene, methylethylketone and cyclohexane for a period of 29 years died of chronic lymphoid leukemia (244).

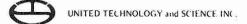
In cases where more moderate exposure to paradichlorobenzene was reported, patients complained of severe headaches, profuse rhinitis and periorbital swelling for approximately 24 hours after exposure.

Anorexia, nausea, vomiting, weight loss and yellow atrophy of the liver were reported for high exposure concentrations.

Heavy use of paradichlorobenzene as either a moth-repellant or a deodorizer has apparently resulted in weakness, nausea, vomiting and jaundice. There are at least two reports of deliberate ingestion of paradichlorobenzene. One woman who developed an appetite for paradichlorobenzene during the first three months of her pregnancy complained of tiredness, anorexia, dizziness and edema of the ankles. She was hospitalized with hemolytic anemia and delivered a healthy child several months later. Another woman who ate 4 to 5 paradichlorobenzene pellets daily for 2-1/2 years complained about increased patchy pigmentation. Unsteadiness and tremors occurred when she stopped taking the pellets, but these symptoms were thought to be due to psychological rather than physiological withdrawal (245).

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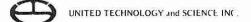
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14 STANDARDS

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#### 14.1 SUMMARY

In Ontario the <u>occupational</u> <u>standards</u> for the chlorinated hydrocarbons of interest here are based on eight hour average concentrations and are usually the same as the TLVs recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).

- methyl chloride	100	(210) ppm $(mg.m^{-3})$
- methylene chloride	200	(720)
- chloroform	25	(120)
- carbon tetrachloride	10	(65)
- l,l,l-trichloroethane	350	(1900)
- 1,1-dichloroethylene	10	(40)
- trichloroethylene	100	(535)
- tetrachloroethylene	100	(670)
- chloroprene	25	(90)
- chlorobenzene	75	(350)
- p-dichlorobenzene	75	(450)

Ambient air standards in Ontario refer to half hour average point of impingement concentrations. Those compounds of concern here which have been promulgated are:

methylene chloride	100 mg.m <sup>-3</sup>
carbon tetrachloride	20
l,l,l-trichloroethane	350
trichloroethylene	85
l.l-dichloroethylene	26

Water quality standards are generally not compound specific and are regulated by such parameters as BOD, COD, TOC, turbidity, etc.

The exception is drinking water in the U.S. which has a maximum concentration standard for trihalomethanes (including chloroform) of 0.10 mg/l or 100 parts per billion. The USSR also lists standards for a number of compounds in drinking water.

#### 14.2 OCCUPATIONAL HEALTH STANDARDS

Occupational health standards are variously referred to as
"Threshold Limit Values" (TLVs), "Time Weighted Averages" (TWAs),
"Short Term Exposure Limits" (STELs), "Maximum Allowable Concentrations"
(MACs), "Maximum Permissible Concentration (MPCs), etc. depending on
the organization issuing the standard or the jurisdication within
which the standard is applied.

In the U.S. there are three organizations which publish standards for sets of compounds. These are the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH) and the American National Standards Institute (ANSI). Standards set by ACGIH are guidelines, updated annually, for occupational exposures. However, OSHA sets occupational standards under mandate of the U.S. Occupational Safety and Health Act (1970) and such standards thus become part of the U.S. law.

OSHA standards are expressed as "Time Weighted Average" (TWA) concentrations, which represent the average concentration of a compound, usually over an 8 hour working day. TWAs are chosen for which almost all workers may be repeatedly exposed, on a long term daily basis, without adverse effects. Notwithstanding TWA requirements, there are often also prescribed "ceiling" levels which are higher concentrations than the TWAs and represent concentrations which may not (except under certain conditions) be exceeded, even for short periods of time. For those compounds for which no ceiling level is given, excursion factors are



applied (based on the TWA) which effectively determines ceiling levels. The ceiling levels may be exceeded only where higher peak levels are allowed. These higher levels are usually limited to a certain concentration which may occur for no more than a defined period of time and a maximum frequency during a working day. For example, the OSHA listed TWA for methyl chloride is 100 ppm (8 hour average) and the ceiling is 200 ppm. This ceiling of 200 ppm may only be exceeded once every three hours, for a duration of no more than five minutes on each occasion and only up to a maximum concentration of 300 ppm.

In addition to the above, OSHA also defines an "action level" as one half of the TWA. Once 8 hour average concentrations reach this "action level", certain monitoring activities are required. It may also be required that additional control measures or other actions be taken, in anticipation of exposures above the TWA, in order to protect workers against such exposure.

The ACGIH defines maximum exposure limits above ceiling levels as "Short Term Exposure Limits", (STEL). These represent the maximum concentration which may occur at any time and such concentrations are limited to a maximum period of 15 minutes. There must be at least 60 minutes between such excursions and no more than four in a given work day.

In Canada, and Sweden the standards usually are 8 hour TWAs, as in the U.S. However, in other countries, such as Germany, standards refer to "Maximum Allowable or Maximum Permissible" concentrations (MAC or MPC).

These are the highest concentrations which can occur in the workplace at any time except where short term excursions above these levels are allowed.

Occupational health standards used in Ontario generally follow ACGIH guidelines.

The current standards for the chlorinated hydrocarbons of concern here for Ontario and the U.S. as set by OSHA and ACGIH are listed in Table 14-1. The most recent standards proposed by OSHA or recommended by the National Institute for Occupational Safety and Health (NIOSH) relevant to these chlorinated hydrocarbons are listed in Table 14-2. Those proposed standards which are set at extremely low levels (less than 5 ppm) reflect suspected carcinogenicity of the particular compound.

Table 14-3 lists occupational health standards for chlorinated hydrocarbons for Sweden and the German Federal Republic (16).



# OCCUPATIONAL STANDARDS FOR CHLORINATED HYDROCARBONS IN ONTARIO AND THE U.S.

(All figures reported in ppm; corresponding mg/m<sup>3</sup> in parentheses)

COMPOUND	ONTARIO		i	UNITED STATES			REFERENCES
			OSHA		A	CGIH	
	8 hr TWA	8 hr TWA	Celling	Peak	8 hr TWA	STEL	
Methyl Chloride	100 (210)	100 (210)	200 (420)	300 (630) (5 min/3 hrs)	100 (210)	125 (260)	2,3
Methylene Chloride	200 (720)	500 (1800)	1000 (3600)	2000(7200) (5 min/3 hrs)	200(720)	250 (900)	2,3
Chloroform Carbon Tetrachloride	25 (120) 10 (65)	10 (48) 10 (65)	50 (240) 25 (160)	200 (1300) (5 min/8 hrs)	25(120) 10(65)	25(120) 25(160)	2,3 2,3
1,1-Dichloroethane 1,2-Dichloroethane 1,1,1-Trichloroethane	 350 (1900)	100 (410) 200 (800) 200 (1085)	 350 (1900)		200 (820) 50 (200) 350 (1900)	250 (1025) 75 (300) 450 (2375)	2,4 2,3 2,3
1,1,2,2-Tetrachloroethane 1,1-Dichloroethylene	10(40)	5(35) 10(40)			5(35) 10(40)	10(70) 20(80)	2,3 2,3
1,2-Dichloroethylene Trichloroethylene	100 (535)	200 (790) 100 (535)	200 (1070)	300 (1605) (5 min/2 hrs)	200 (790) 100 (535)	250 (1000) 150 (800)	2,3,5 2,3
Tetrachloroethylene	100 (670)	100 (670)	200 (1340)	300 (2010) (5 min/3 hrs)	100 (670)	150 (1000)	2,3
Chloroprene Chlorobenzene o-Dichlorobenzene p-Dichlorobenzene	25 (90) 75 (350)  75 (450)	25 (90) 75 (350)  75 (450)	50 (300)		25 (90) 75 (350) 50 (300) 75 (450)	35(135) 75(350) 50(300) 110(675)	2,3 2,3,4 2,3,6 2,3,7

# OSHA/NIOSH PROPOSED STANDARDS FOR OCCUPATIONAL EXPOSURE TO CHLORINATED HYDROCARBONS

COMPOUND	$pom (ma/m^3)$	REFERENCE
Methylene Chloride <sup>a</sup>	76(261) 10 hr TWA	8
Chloroform	2(9.9) 1 hr sample	9
Carbon Tetrachloride	2(12.6) 1 hr sample	10
Ethylene Dichloride	5(20) 10 hr TWA 15(60) Peak, 15 min/10 hrs	11
1,1,2,2-tetrachloroethane	1(6.87) 10 hr TWA	12
Trichloroethylene	100(535) 8 hr TWA 150 (800) Ceiling	13
Tetrachloroethy lene	50(339) 10 hr TWA 100(678) 15 min., twice daily	14
Chloroprene	(3.6) Peak, 15 min., 8 hr.	15

# THRESHOLD LIMIT VALUES FOR

#### CHLORINATED HYDROCARBONS

## IN SWEDEN AND GERMANY (16)

4	THRESHOLD LIMIT V	ALUE
COMPOUND	SWEDEN	GERMANY
	8 nr TWA, ppm (mg/m <sup>3</sup> )	MPC, ppm $(mg/m^3)$
Maranal Chilosoft		/
Metnyl Chloride		50 (105)
Metnylene Chloride	100 (350)	500 (1750)
Chloroform	25(120)	50(240)
Carpon Tetrachloride	10(65)	10 (65)
1,1-dichloroethane	) <del>=0=</del>	100 (400)
1,2-dichloroethane	20(80)	20(80)
1,1,1-trichloroethane	100 (540)	200 (1080)
1,1,2,2-tetrachloroethane		1(7)
l,l-dichloroethylene		200 (790)
1,2-dichloroethylene	in in	
Trichloroethylene	30 (160)	50 (260)
Tetrachloroethylene	30 (200)	100 (670)
Chloroprene	25(90)	25 (90)
Chlorobenzene		50(230)
o-dichlorobenzene		50 (300)
p-dichlorobenzene	<del>==</del>	75 (450)

## 14.3 AMBIENT AIR STANDARDS

Several countries have regulations governing ambient air concentrations of certain pollutants, such as sulfur dioxide, nitrogen oxides, particulate matter, and total hydrocarbons. Chlorinated hydrocarbons are normally considered within the class of total hydrocarbons, and standards have not been set on a compound-by-compound basis. In certain jurisdictions within the U.S. (eg Los Angeles County Air Pollution District, Rule 66), emissions of photochemically reactive compounds are restricted. However, current thinking within the U.S. is to consider all hydrocarbons, except possibly methane, as photochemically reactive and thus to restrict emissions of all hydrocarbons, which essentially moves away from the principle of compound-specific standards (1).

In contrast, Ontario sets compound-specific half hour average point of impingement standards, which include several of the chlorinated compounds of interest. These point of impingement standards are set out in Regulation 15, Schedule 1, of the Revised Regulations of Ontario under the Ontario Environmental Protection Act. The current version of Regulation 15, Schedule 1 dates from June 1st, 1977. Those point of impingement standards for chlorinated hydrocarbons of interest here are listed in Table 14-4.

None of these chlorinated hydrocarbons are presently listed as part of the Ontario Ambient Air Quality Criteria (17).

# ONTARIO HALF-HOUR POINT OF IMPINGEMENT STANDARDS FOR CHLORINATED HYDROCARBONS

COMPOUND	STANDARD µg/m3
Methylene chloride	100,000 (½ hr. Avg.)
Carbon Tetrachloride	20,000
l,l,l-trichloroethane	350,000
Trichloroethylene	85,000
l,l-dichloroethylene	26,000

#### 14.4 WATER STANDARDS

The US EPA has recently introduced a drinking water standard for concentrations of trihalomethanes, which includes chloroform (18). This standard sets a "Maximum Contaminant Level" (MCL) of 0.10 mg/i (100 parts per billion) for total trihalomethanes, including chloroform, which occur in drinking water as the result of the interaction of the chlorine applied for disinfectant or other purposes, with the organic substances which naturally occur in raw water. The only other country that has been found to set compound-specific drinking water standards for chlorinated hydrocarbons is the USSR. These standards are listed in Table 14-5 (19).

Generally current standards are regulations governing effluents by such parameters as BOD, COD, TOC, turbidity, fish toxicity, etc.

#### MAXIMUM PERMISSIBLE CONCENTRATIONS OF CHLORINATED

# HYDROCARBONS IN DRINKING WATER IN THE USSR (19)

COMPOUND	MAXIMUM PERMISSIBLE CONCENTRATION
	(mg/1)
Methylene chloride	7.5
Carbon tetrachloride	0.3
Trichloroethane	0.5
Tetrachloroethane	0.2
Chlorobenzene	0.02
Dichlorobenzene	0.03
o- and p-dichlorobenzene	0.002

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